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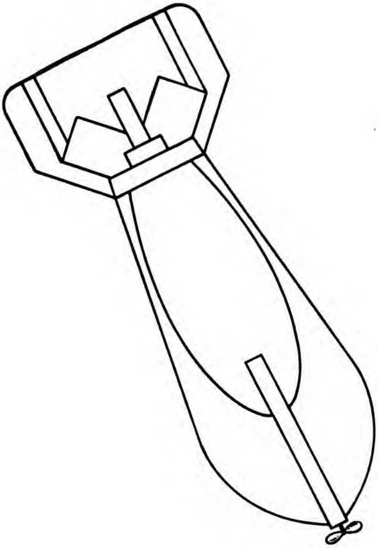

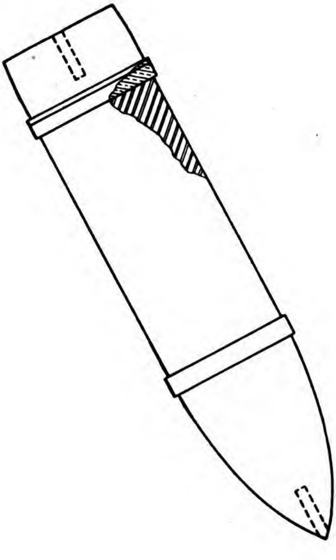

EXPLOSIVES

An Introduction to Their Chemistry, Production, and Analysis

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THOMAS Y. CROWELL COMPANY
New York

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Preface

THERE IS no deficiency of excellent literature in the field of explosives. There is, however, an absence of material of this kind written in relatively simple and readable style and assembled in one book. To furnish such a single source of information on the science of explosives is the principal purpose of this work.

In developing that purpose, the author has attempted to emphasize a fundamental and practical viewpoint, and to avoid the tendency to make it a textbook of synthetic organic chemistry or a treatment of special topics in organic chemistry. This latter information is readily accessible in other books, whereas that set forth here is not. The descriptive material presented is highly condensed, but the worth-while student will locate the other corners from those described.

For at least two good reasons, very new developments are not treated at length. First, such discoveries and inventions are readily understood by one versed in fundamentals when he comes in contact with them. Second, many of the current "revolutionary" and secret discoveries—about which the writer does not profess to have restricted information but which have been publicized in sufficient detail that their basic principles are fairly apparent to anyone familiar with the field—will later prove to be much less startling and important than their present build-up makes them appear. Even though the explosive field today does, of course, exhibit the accelerated pace of change seen in all fields of technology which have received the impact of the war, revolution is not in general characteristic of scientific progress and is no more likely in this field than elsewhere in science.

It may be said that in this book the descriptions of specifications for certain military explosives and accompanying analytical procedures, and of certain military devices follow United States government literature quite closely. No apology need be made for that. The sources are clearly indicated, and the similarity is a guarantee that the information is authentic and conforms with the requirements of

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one of the most important outlets for explosives. On the other hand, the liberty of making certain types of changes has been taken, as, for example, modifications of language for the sake of greater clarity, of terminology to conform with other usages, and of laboratory directions where it was thought to be helpful.

It should be observed in passing that the sections on "Discussion Questions and Exercises" at the close of each chapter contain some questions designed to relate the study of the field of explosives to other training the reader may have had. It will therefore be futile to look in this volume for answers to every one of the questions and exercises because in some cases answers are not provided. Such instances will, of course, be obvious to anyone who has read the material with reasonable thoroughness and understanding.

The writer wishes to express his appreciation of the co-operation which he has everywhere received in the labor of preparation. He is especially grateful to those who have prepared those United States War Department technical manuals and literature upon which he has drawn freely, to the officers in the services, to several explosive manufacturers, and to Mr. Michael Heller, all of whom have been able to provide materials of various kinds generously; to the explosive and instrument manufacturers and technical publishers who have graciously extended permission to use illustrations, charts, and tables; and to Mr. David Sharefkin, Dr. Alexander Calandra, and Mr. S. Gerald Hinden for their assistance in the development of our course at the Brooklyn College. Finally, to all of those, who must necessarily be nameless, who have contributed to the infinity of details involved in a task of this nature, and whose aid in a more personal way remains a pleasant memory in the mind of the writer, he also extends sincere thanks.

Martin Meyer

Brooklyn, New York
May, 1943

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CHAPTER 1

A General Survey

The Chemistry of Explosives. In view of the development of the science of chemistry in the United States, explosive chemistry is a topic which, save in a few technical schools, has received relatively little educational attention here. The association of explosives with war and the American distaste for things military are probably the principal reasons for this indifference. As thoughtful a writer as Kendall[1] in citing the value of chemistry to the modern world classifies explosives "on the destructive side." Yet explosives undoubtedly rank with the greatest discoveries man has ever made; and although they are notoriously applied to war, explosives are just as closely applied to the arts of peace. Without explosives, modern engineering achievements would be infinitely more difficult, if not impossible. They are also closely linked to the development of modern chemistry: Lavoisier was chief of the arsenal at Paris; Berthelot, Bunsen, Castner, Haber, van't Hoff, Landolt, Le Chatelier, Mellor, Mitscherlich, Nernst, Ostwald, Rumford, and many others whose names are famous were expert in the field.

Early Explosives. Gunpowder, or black powder as it is now commonly called, was the first explosive. It came into use in England early in the fourteenth century, although there is mention of its application by the Turks during a siege in 1273. The discovery of gunpowder is usually credited to Friar Roger Bacon (1214?–1294), but some authorities award the honor to a Teutonic monk, Berthold Schwarz to whom there is a monument at Freiburg, Germany. When he lived is a bit uncertain, but he appears to have been born a little earlier and to have been living during Bacon's time. There is a legend of an earlier Chinese discovery, and also the possibility that gunpowder goes back to the Hindus. The Chinese are still expert in the manufacture, by primitive manual operations in the main, of some pyrotechnic (fireworks) devices which utilize gunpowder mixtures. Gunpowder seems a natural outcome of "Greek fire," essentially a nitrate and pitch mixture, in use as early as the eighth century, and it may have been more or less contemporary with the discovery of nitrates. Davis[2] gives an interesting historical sketch.

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[1] Kendall, *Smith's Inorganic Chemistry*, 2nd rev. ed., p. 647.

Although many improvements in gunpowder were made,[3] it remained the only practical explosive until the nineteenth century, when the forerunners of modern high explosives were developed. Of these, nitroglycerine, discovered by the Italian, Ascanio Sobrero (1812–1888) in 1847, was initially the most important. A portion of his original preparation, it is said, is still preserved in a factory at Turin where a part is tested annually. Together with nitrocellulose, discovered by T. J. Pelouze in 1838, nitroglycerine probably is still most important, especially commercially, although many others today have a variety of values.

The development of nitroglycerine into a practically useful explosive, as well as the discovery of many other important phenomena, was the contribution of the Swedish genius, Alfred Nobel (1833–1896) who may well be considered the father of the science of explosives. Among his achievements were theories of explosive action, the art of initiation by detonation of high explosives to secure their full power, and many useful explosives of which dynamite is probably the best known. Nobel was an exceedingly practical man, as well as one with a brilliant scientific mind. He protected his work with hundreds of patents in all the countries of the world, founded an international industry in the manufacture of explosives, and amassed a great fortune, part of which at his death he devoted to the establishment of the now famous Nobel Prizes.

Among the many others associated with pioneer work on explosives during the nineteenth century, certain men made outstanding practical contributions: the German chemist C. F. Schoenbein who worked on nitrocotton and is sometimes credited with its discovery (1846); General T. J. Rodman, who studied the size and shape of gunpowder "grains" (1860) and made discoveries which still are basic for the manufacture of propellent powder; Sir Frederick Abel (1827–1902) in England who made the large scale manufacture of nitrocotton practicable by doing it; and the French chemist P. M. E. Vieille who first gelatinized nitrocotton with alcohol and ether mixture as a solvent to make smokeless powder (1886).

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[2] Davis, Tenney, *The Chemistry of Powder and Explosives.*

[3] *Vide* early references in the Bibliography, Appendix.

Explosives in War. The first extensive use to which gunpowder was put, as a boudoir lordling in Shakespeare[4] laments, was to the propulsion of projectiles from suitably designed machines intended for military purposes. There are a few previous uses recorded, but it is usually agreed that the first open-field use of artillery was by the English at the battle of Crécy in 1346. Early guns were crude and clumsy affairs, but improvements have been continuous, rapid, and interesting. Projectors have evolved in the diverse directions of hand weapons and larger types, and various inventors have concentrated on design, on methods of loading the charge and missile, on methods of firing, and on rate of fire. Modern guns are among the most remarkable examples of man's mechanical ingenuity.

Today the use of explosives is an even more extensive science than their chemistry. Projector devices may be classified as small arms, artillery, and numerous special devices. Small arms (under 20 mm. caliber) include pistols of various kinds, rifles, machine guns, and others; artillery is of greater caliber. Artillery pieces may be mobile, on mounts drawn by man, horse, automobile, tractor, or railroad, or maybe fixed, as in coast or naval artillery. The most familiar characteristic of the projector is the diameter of the bore, or caliber, which may be expressed in any convenient units. The smallest calibered projectors are miniature pistols suitable for watch charms, and some familiar small-arms calibers are .22, .30, .32, .38, .45, and .50 inch. Familiar cannon calibers are 37, 75, 90, 105, 155 mm., and 3, 5, 6, 8, 10, 12, 14, 16, and possibly 18 inches. The standard caliber for a police revolver is .38, for the army automatic pistol .45, for the army rifle .30 inch. A large field artillery weapon is a howitzer 10 inches in caliber; an important antiaircraft gun is 3 inches, and the largest cannon now used in the U. S. Army is 18 inches, in caliber. For the specialist, not only the caliber, but every feature of design is important—material, thickness, capacity of powder chamber, length of bore, gross weight, design of projectile, and the like.

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[4] Shakespeare, *King Henry IV*, First Part, Act I Scene 3—Hotspur:

"And that it was a great pity, so it was,
This villanous saltpetre should be digg'd
Out of the bowels of the harmless earth,
Which many a good tall fellow had destroy'd
So cowardly; and but for these vile guns,
He would himself have been a soldier."

In addition to the projector, the projectile may itself contain explosive charges, although the general use of explosive bullets for small arms is forbidden by the international rules of war. An extensive modern military use of explosives is in grenades and bombs of all kinds which may be thrown by hand or by infantry mortars and special projectors, dropped by airplanes, placed by engineers, or dropped overboard from ships for use against submarines. Improvements in the art of using explosives have resulted in a wide diversity of materials and methods which have both general and special application. Modern war may quite properly be said to be largely the science of the use and distribution of explosives.

Explosives in Peace. But quite apart from military application, the explosive has a very important place in modern civilization. For several centuries explosives have been used in mining coal. More recently, new uses have developed rapidly. Today explosives are in daily use in coal mining; in metal mining of all kinds; in quarrying and non-metallic mineral mining; in railway and other construction work such as roads, dams, building foundations, pipe lines and oil-well drilling; in clearing land of rocks and stumps; in ditching; and in demolition work both on land and under water. In fact, almost no modern engineering undertaking can dispense with explosives.

The United States Department of the Interior classifies the explosives produced in the United States under the headings of black blasting powder; permissible explosives (that is, explosives which have passed certain tests of the United States Bureau of Mines and may allowably be used in gassy or dusty mines, which implies certain properties, provided that they are also used in the manner specified by the Bureau); and high explosives, which includes all others. Table 1[5] shows United States production for the years 1912 to 1940, but as early as 1904 the United States had produced 347 million pounds.

While hundreds of materials function as explosives, the large-scale industrial explosives are relatively few in number. The important military explosives are black powder, smokeless powder (basically

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[5] Adams, Wrenn, and Horton, *Production of Explosives in the United States—1940.* U. S. Govt. Tech. Paper 636.

TABLE 1

EXPLOSIVE PRODUCTION IN THE UNITED STATES

(millions of pounds)

Year	Permissible Explosives	High Explosives	Black Powder	Total
1912	25	235	230	489
1913	28	242	230	500
1914	26	218	206	450
1915	27	236	198	461
1916	35	255	216	505
1917	43	262	277	582
1918	46	206	247	499
1919	39	198	181	418
1920	54	229	255	538
1921	41	171	160	372
1922	43	210	179	432
1923	60	267	202	530
1924	55	273	167	496
1925	58	286	157	502
1926	68	311	158	536
1927	64	303	132	499
1928	61	293	122	475
1929	63	327	120	510
1930	54	291	100	445
1931	42	216	80	338
1932	32	138	64	234
1933	34	158	64	256
1934	39	207	69	315
1935	39	200	69	308
1936	48	262	82	392
1937	50	289	66	405
1938	42	239	62	342
1939	50	278	58	386
1940	58	305	60	423

nitrocellulose), trinitrotoluene, amatol (a mixture of trinitrotoluene and NH_4NO_3), ammonium picrate, nitrostarch, tetryl, picric acid, and the initiating explosives mercury fulminate and lead azide. The important commercial explosives are black powder, dynamite (basically nitroglycerine), blasting gelatin (basically nitroglycerine and nitrocellulose), ammonium nitrate, and for initiation fulminate of mercury and, to some extent, tetryl and P.E.T.N. (pentaerythrite tetranitrate). In Table 1, the production figures include black powder for both war and peace uses; permissible explosives are completely limited to peaceful uses; and high explosives include both types. The figures also may not include some ammunition manufacturing, and do not indicate the total capacity. One explosive firm estimates U. S. annual production of dynamite alone at 350 million pounds. It is estimated that the total United States capacity for 1940 was 623 million pounds.

During 1940, coal mining used 89% of the black powder produced, 99% of the permissible explosives, and 8.7% of the high explosives. All classes of mineral operation accounted for 63% of the high explosives, and construction work took 33.5%. These uses, which are clearly peaceful applications, may not include all, but nevertheless account for over 95% of the total recorded United States production in 1940. These uses also present specialized problems for which military explosives are not all adapted. Many modern explosives have been developed to meet this demand. For these purposes explosives are used in bulk or in special forms suitable to the application.

The Manufacture of Explosives. It is clear that explosives enter into modern life on a very large scale. A first-class nation may annually use as much as 300,000 tons in peace, and this figure may rise to 3,000,000 tons or more in war. In fact, in modern war, availability is about the only upper limit. During the First World War, the initial American program for munitions called for the annual production of 3,000,000 tons of NH_4NO_3 alone; this planned production was never completed, and the now famous and obsolete Muscle Shoals plant is the only remainder from it. What was done is now history.[6] In the early part of the Second World War, Britain's failure to bomb Germany on a scale comparable to her own suffering was due as much to a lack of explosives as to a lack of airplanes, but by the spring of 1942 she was using as much as 3,000 tons in a single raid. Nevertheless, Germany's admitted capacity of 1,500,000 tons annually, which may be several times larger, remained a tremendous advantage, and an outstanding feature of the otherwise colossal American war program is the apparent underestimate of explosive requirements, as indicated by the published figures.

Manufacture of explosives is, as suggested by the figures mentioned, an industry to be conducted on a large scale and any explosive must lend itself to such operations if it is to be practically useful. Materials which are very sensitive are thereby eliminated from practical consideration, except for very specialized purposes, or limited to use on a small scale. Modern high explosives cannot be, therefore, and are not especially sensitive under ordinary circumstances. But their manufacture is always hazardous, sometimes extremely so, and is conditioned by extensive precautions which have been largely taught in the past by costly experience. Even so, the behavior of explosives is in some respects rather describable statistically than exactly, and that of a given sample may depart widely from the average for reasons not

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[6] See *America's Munitions—1917–1918*, U. S. Govt. Printing Office.

TABLE 2

MANUFACTURERS OF EXPLOSIVES IN THE UNITED STATES (1940)

Name	Location*	Product†
Allied Chemical and Dye Corp.	Hopewell, Va.	H
American Cynamide and Chemical Corp.	New York, N. Y.	H, P
Apache Powder Co.	Benson, Ariz.	H
Atlas Powder Co.	Wilmington, Del.	B, H, P
Austin Powder Co.	Cleveland, Ohio	B, H, P
Columbia Powder Co.	Tacoma, Wash.	H, P
E. I. Du Pont de Nemours & Co., Inc.	Wilmington, Del.	B, H, P
Egyptian Powder Co.	East Alton, Ill.	B
Equitable Powder Manufacturing Co.	East Alton, Ill.	B
Grange Powder Co.	Seattle, Wash.	H
Hercules Powder Co.	Wilmington, Del.	B, H, P
Illinois Powder Manufacturing Co.	St. Louis, Mo.	H, P
Imperial Explosives Co.	Kansas City, Kansas	H
Independent Explosives Co.	Cleveland, Ohio	H
Kelbar Powder Co.	Wilmington, Del.	H
The King Powder Co., Inc.	Cincinnati, Ohio	B, H, P
Liberty Powder Co.	Pittsburgh, Penn.	H, P
National Powder Co.	Eldred, Penn.	H, P
New York Glycerin Co., Inc.	Bolivar, N. Y.	H
Texas Torpedo Co.	Electra, Texas	H
Titan Explosives Co., Inc.	Portland, Oregon	H
Trojan Powder Co.	Allentown, Penn.	H
United States Powder Co.	Terre Haute, Ind.	B
West Coast Powder Co.	Everett, Wash.	H
Western Powder Manufacturing Co.	East Alton, Ill.	B
Zenith Powder Co., Inc.	Oregon City, Oregon	H

* These are not plant locations in all cases.

† B = black powder, H = high explosives, P = permissibles.

always clear. The relatively small number of accidents in the industry should be a cause of more interest than the actual number.

Availability and cost of starting materials are important considerations in the adoption of an explosive. One of the reasons usually given for the development of a straight nitrocellulose propellant for the United States Army, which became regulation about 1909, was the thought that glycerine for nitroglycerine might be difficult to obtain on a large scale; this foresight proved to be sound in 1917, although it has less application today.

Location and design of plants for manufacturing explosives is conditioned by a variety of factors which are not altogether chemical; for example, nearby civilians and civilian activities which might be endangered; military considerations of attack, which introduces such disputes as the large plant versus many small ones; and geographic distribution of raw materials such as power, coal, nitrogen, and others. Table 2 presents some of the principal manufacturers of explosives in the United States in 1940, and their products. As part of the war program, the United States government has built many explosives plants as well as aided private companies to enlarge their capacities.

Handling and Storage of Explosives. The keynote of all actual work with explosives—in the laboratory, the factory, and the field—must be safety. Rules must be learned and they must be obeyed. With the best of foresight, explosive behavior is sufficiently unpredictable that it certainly does not pay to face a known risk. In wartime the handling of explosives in the United States comes under the Federal Explosives Act of December 26, 1941 (Public, No. 381, 77th Cong.), which is administered by the United States Bureau of Mines, and there are also local and federal laws concerning various aspects of the situation.

Before undertaking any work at all with explosive materials the person in responsible charge must familiarize himself with the various legal requirements and comply with them, and also with the general and special safety precautions that apply to his particular job. These matters will be discussed in some detail at appropriate places.

Explosives are not as a rule used immediately after manufacture, and, particularly for military purposes, may have to be stored for long periods, sometimes years. They must consequently be chemically reasonably stable to moisture, air, and climatic temperature changes, as well as amenable to moderate handling and to storage without too much risk. Careful routines are worked out for inspection, testing, and storage; practical selection is often made on the basis of these considerations. This must be borne in mind in working with other materials. Military explosives are often stored in the field under conditions where they may be hit by projectiles and subject to other fortuitous circumstances against which, under more usual conditions, they might be protected. This condition suggests that one criterion for military explosives is that they must be somewhat more rugged than others. Safety precautions must be adjusted to suit the needs of the specific situation—laboratory, plant, or field.

The final step in the application of explosives is to fire them. This operation is a more difficult one than might be thought, if the explosive is to be used at maximum efficiency, though it is worth remembering that serious accidents can occur through discharge at inappropriate times even at minimum efficiency. Some explosives may be fired by a sharp blow or percussion and some by heating. Heat may be applied by a flame or by a spark electrically produced, or by heat from mechanical friction. Various explosives that are not easily fired in these ways may be employed in practice in conjunction with a small amount of another explosive that may be so fired, in a device known as a primer or detonator. As the explosives in these primers or detonators are more sensitive than the principal charge, these devices must be handled with even greater care, and their charges are made as small as circumstances permit. The weight of such charge required for maximum efficiency is related to the weight of the main charge. To reduce the amount necessary, a smaller amount may be used to fire an intermediate more stable explosive known as a "booster," which in turn induces the explosion of the main charge. An actual explosive device may therefore be a combination of several chemically different explosives, as well as of complicated mechanical arrangements to achieve the desired results, and the chemical arrangement is referred to as the explosion train.

Other characteristics of practical explosives may be determined by special conditions of use. In coal mines which contain fire damp or excessive coal dust, an explosive with too high an explosion temperature, or too large or persistent an explosion flame may cause a gas or dust explosion, and the permissible explosives already mentioned were developed to meet this situation. Sometimes opposite characteristics are both useful—excessive smoke in a propellent explosive is objectionable because it indicates too easily the source of a shot, but bullets containing explosive materials which leave a smoke trail, known as tracer bullets, are useful. Excessive flash is objectionable for military firing at night; toxic fumes as a residue of explosion are dangerous under some conditions but may be desirable in others; water resistance and other properties must be considered.

Under all conditions of use a certain incidence of accidents is inevitable (see Table 3); and even in wartime only a very small proportion of the accidents can be charged to overt negligence or sabotage, although systematic programs of safety produce very encouraging results. In practical use in mining and construction, the principal causes of accident include such things as careless transportation; improper charging and tamping; premature blast due to short fuse, stray currents, or other causes; shots breaking through; drilling into old holes; sparks from matches or smoking materials; open or mud-capped shots; suffocation from fumes; thawing of dynamite; caps and detonators; and returning too soon. In the plant and laboratory other causes operate.

TABLE 3

ACCIDENT RATES FOR MINES AND QUARRIES

(per million man-hours of employment)

Year	Fatal	Nonfatal
1935	.089–.203	.768– .903
1936	.079–.234	.665–1.071
1937	.068–.202	.836– .980
1938	.067–.192	.489–1.054
1939	.072–.107	.675–1.093

Laboratory Work. The consideration of explosives brings to a focus a number of sciences—mathematics, physics, engineering, chemistry, and others. As in any other chemical science, understanding requires actual laboratory contact and systematic experimentation. Some important types of experimental work demand large-scale apparatus and routines which are conducted of necessity on proving grounds such as the famous one at Aberdeen, Maryland, or the new one being built in conjunction with the United States Military Academy at West Point. Both types of experimentation will be described in so far as they have chemical relations.

An elementary explosives laboratory may have about the same general equipment of work tables, hoods, and reagents as any other chemical laboratory. It should also have chemical balances suitable for the number of students. These balances should be in a separate room, which may also be utilized for some experiments which are too sensitive to be carried out in the presence of fumes common to a laboratory. A balance of the usual type suitable for quantitative work and sensitive to 0.1 milligram is satisfactory. While some interesting studies of microchemical procedures in explosives work are beginning to appear,[7] they are not yet standard in the field. In addition to the specialized apparatus which will be described, the laboratory should have as part of its equipment a good adjustable-temperature electric drying oven, a thermostat, a muffle furnace, electric steam bath, and hot plate, as well as conveniently located electrical outlets for other apparatus. Electric heating devices should have covered, not exposed, heating elements. Because of the fire hazard, perhaps ideally all heating in the explosives laboratory should be electric or steam, so that the usual no-matches rule may maintain, but this is not absolutely necessary provided that other appropriate precautions are enforced. There should be adequate storage cabinets (but ***not*** for explosives!!) and some instructors will prefer having at least part of the laboratory set up as "stations" for permanent apparatus to which the student goes to perform his experiment. Some of the highly specialized explosives apparatus is not generally available, and for introductory work may be avoided. This consideration has influenced selection herein.

In the student laboratory (read Chapter 18, especially page 429) it is important at all times to be familiar with the specific characteristics of the materials being handled. One should always consider the general hazards of student thoughtlessness, carelessness, and negligence. The eyes should always be protected. Experiments may often be conducted behind laboratory-size barricades of fiberboard or metallic plates. Cleanliness should be enforced and handling of materials in contact with the skin should be minimized, as many explosive materials have toxic reactions which may be severe in individual cases. There is always a risk of induced explosion when explosives begin to accumulate in lockers and cabinets.

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[7] Elving and McElroy, *A Du Pont Type Semimicro Nitrometer* J. I. E. C., Anal. Ed., January 15, 1942.

A practical course should include an organized and representative sampling of laboratory experiments on explosives and related materials involving the determination of physical properties such as melting point, density, viscosity, and chemical properties, as well as special properties not usually determined for other materials; synthesis of the chemical substances, as well as the preparation of practical materials, of course, after careful emphasis upon the safety precautions imperative in each operation; and analysis and testing according to practical specifications of raw materials, semifinished, and finished products. Wherever possible the material used should be the real thing. At least one exercise in actual use should be projected.

Each experienced instructor will have his own ideas as to what to present since this field presents no general agreement as yet, and this volume will enable some choice to be made. Some of the given methods of synthesis are adaptations from the usual commercial methods of production, rather than ordinary laboratory processes, which is purposefully done to emphasize the nature of the practical procedures. The quantity and nature of the work done will be to some extent determined by the number and distribution of hours in the course allotted to lecture, recitation, and laboratory.

A list of the subjects of lecture, recitation, and laboratory periods, prepared in advance for the student, is useful. As a first laboratory exercise it is suggested that the student calibrate his balance for full-range sensibility and also calibrate and standardize his weights and such other quantitative apparatus as melting-point thermometers and burettes, and review the elementary principles of precision measurement, following the procedure given here or that of any standard text of quantitative analysis. Reports of all experimental work should be carefully written out later, and examined and corrected by the instructor. A standardized report form covering method, apparatus, observation, summary, and discussion of results is preferred by the writer. It is also important to provide access to a good library and to require the student to obtain as much collateral information on each topic as his time permits.

Safety is of prime importance in the laboratory as elsewhere. Specific mimeographed rules for conduct in the laboratory, based upon knowledge and consideration of the actual arrangements of the laboratory, should be given to each student and also posted on a laboratory bulletin board. It will lend atmosphere if on this board are posted, from time to time, available commercial leaflets on safety campaigns and safety related to explosives, blasting caps, and the like. Students must wear goggles or safety masks at all times.

While actual explosive materials should be employed as far as may be possible, these should not be stored in the general laboratory even in temporary reagent bottles, but kept in a distant center accessible to only one person (preferably the instructor) and handed out by him to individuals in the quantities necessary. The student should be taught to use only the minimum amount required for the experiment; and if he must keep materials in his desk he should be taught and required to keep them in accordance with approved storage methods until ready for use—for example, under water for nitrocellulose. Residues should be regularly collected by the instructor and destroyed by approved methods. This is especially important at the end of the course, when no material should be left in the student's possession.

As a separate part of every laboratory experiment, the instructor should carefully go over any pertinent safety precautions, and, until by actual knowledge he acquires confidence in an individual, he should supervise in person every hazardous experiment. It is usually well to have only one such experiment proceeding at a time. Students should be warned to perform only experiments which they are directed to perform, and the instructor should know at all times exactly what experiment each student is performing. Under no circumstances should any student be permitted to do any sort of original work on explosives in the same laboratory with a class of students doing routine work; no other courses should be mixed with an explosives laboratory course; and "visiting" in the laboratory should be prohibited.

Preliminary Laboratory Operations. One type of chemical balance is shown in Figure 1. For careful work it is recommended that zero points be determined by the method of swings, using 5 successively, starting with a left swing and estimating the pointer position to the nearest $\frac{1}{10}$ division. Similarly, the sensibility method of weighing should be used, calculating weights to five decimal places. The fifth place is not completely reliable, but it does confirm the fourth. This will be modified by the type of balance used and the nature of the work.

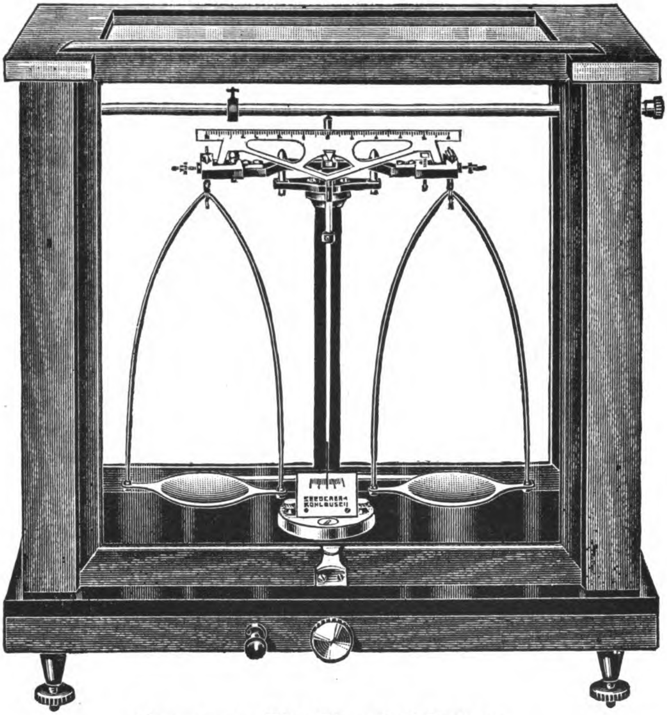

FIGURE 1: **The Chemical Balance**
(Courtesy of Seederer-Kohlbusch, Inc.)

The sensibility of a balance is defined as the weight necessary to displace the zero point one scale division. For balances of this type it will be around .0005 gram. It is determined by placing equal weights (as marked) on the pans, and then an excess weight on one pan by means of the rider placed on the 1- to 3-milligram marks as the position of the zero point permits, and observing the displacement of the true zero point. The sensibility should be determined for load intervals of 10 to 20 grams over the working range of the balance, plotted as a curve on paper, and mounted within the balance case. Weighings may then be made thus:

1. Weigh the object as closely as possible with weights, and place the rider in a position such that the zero point will be on the scale. Record the indicated weight.
2. In this position, determine the zero point.
3. Subtract this zero point from the true zero point, that is, with no load or equal load.
4. Multiply this difference by the sensibility, taken from the graph for that approximate load.
5. Add or subtract this correction from the recorded weight (1) as indicated by the relative position of the zero point.

Only (1) and (2) are observations; calculations may be made later as convenient. With practice this method of weighing is rapid and precise although there are many others.

A set of weights may be calibrated by the scheme tabulated below. To begin, the .01′ weight is placed on the left-hand pan (weights smaller than .01 gram are not calibrated or used), a 10-milligram rider is placed at 10 on the rider arm, and the correction is determined by the zero point. This gives the apparent weight of the .01′ gram weight on the assumption that the rider, as placed, is exactly 0.00100 gram, by adding or subtracting the correction. Each weighing, as indicated in columns 1 and 2 modified by the composition of the box of weights, is made and the correction recorded. Column 4 is calculated for each weight in column 1 successively, by adding the apparent weights of those used in column 2 and adding or subtracting the correction. Column 5 is the weight of each weight on the assumption used here that the 10′ weight = 10.00000 gram and is obtained in each case by the ratio

$$\frac{\text{apparent weight of that weight}}{\text{apparent weight of } 10' \text{ gram weight}} \times 10.$$

Column 6 is the weight in column 5 minus the marked weight, and gives the correction to be employed when that weight is used. These corrections may be tabulated on a card and kept in the weight box. They are, of course, relative, but may be made absolute by calibrating the assumed weight, here 10′ grams, against a standard.

Such careful procedure, and this applies to most calibration when using reliable equipment, is usually not necessary, but in general all

CALIBRATION OF A BOX OF WEIGHTS

1	2	3	4	5	6
Left-hand pan, weight	Right-hand pan, weights	Correction	Apparent weight	Weight relative to 10′ grams	Correction of marked weight
.01′	10-mg. rider at 10				
.01″	.01′				
.02	.01′, 01″				
.05	.01′, 01″, .02, R_{10}				
.1′	.01′, .01″, .02, .05, R_{10}				
.1″	.1′				
.2	.1′, .1″				
.5	.01′, .01″, .02, .05, .1′, .1″, .2, R_{10}				
1.0′	as before +.5				
2.0′	as last +1.0′				
2.0″	2′.0				
5.0	1, 2′, 2″				
10′	1, 2′, 2″, 5			10.00000	
10″	10′				
20	10′, 10″				
50	1, 2′, 2″, 5, 10′, 10″, 20				

work should be done to yield results to four significant figures, with the incidental precision required therefor. To work more precisely than circumstances require or permit is not only bad scientific method, but a waste of time. However, work frequently arises which requires more than usual precision and it is a time saver if one is prepared for it.

Pipettes and volumetric apparatus may be calibrated by weighing the delivered quantity of distilled water. Burettes may be calibrated similarly, at 10 cc. intervals. For temperatures around 20°C., temperature may be neglected. Thermometers may be calibrated by melting point-determinations of standard substances at reasonable intervals. In general the habit of using all graduated scales to estimated tenths of the last division should be cultivated, and home made verniers are of use in this connection.

Role of the Explosives Chemist. From the statistics of the magnitude of the industry, it is clear that chemists with this type of training can find employment for their talents at all times. During war periods, the demand exceeds the supply, and salaries tend to rise or required qualifications to fall. The usual field of employment includes analysts, inspectors, plant control and management, and re-

Title	Salary	Some Requirements
Junior Inspector of Powder and Explosives	$1,620	18 semester hours in organic chemistry
Assistant Inspector of Powder and Explosives	1,800	As for Junior Inspector plus ½ year of experience
Associate Inspector	2,000	As for Junior Inspector, plus 1 year experience
Inspector	2,300	As for Junior Inspector plus 1½ years
Senior Inspector	2,600	As for Junior Inspector plus 2 years
Junior Technologist	2,000	Baccalaureate degree
Assistant Analytical Chemist Assistant Chemist Assistant Research Chemist Assistant Technologist	2,600	Baccalaureate degree plus 2 years experience
Associate, all above titles	3,200	Baccalaureate degree plus 3 years experience
Analytical Chemist Chemist Research Chemist Technologist	3,800	Baccalaureate degree plus 5 years experience
Senior, all above titles	4,600	Baccalaureate degree plus 6 years experience
Principal, all above titles	5,600	Baccalaureate degree plus 7 years experience

search, but there are many incidental fields as well as related ones. At present, chemists with only a moderate knowledge of explosives are useful as instructors of air raid wardens; the service they render is a very real one although not remunerative. In the United States, in addition to private industry, the large employers include the Civil Service both locally and nationally and the Army and Navy Ordnance Departments. Knowledge in the explosives field is also valuable to certain officers in all branches of the military services.

Civil Service positions for which a knowledge of the chemistry of explosives is part of the qualifications today are shown in the preceding table. Full information can be obtained from the United States Civil Service Commission, Washington, D.C. Recently women have been made eligible for many of the posts.

Discussion Questions and Exercises

1. Prepare a brief biography of any of the chemists named in the chapter and indicate their important contribution to explosive chemistry.

2. Plot curves of the trend of explosive manufacture in the United States. What would your prediction be for the present and immediately future years?

3. Find out what has been published on the American explosive programs in 1917 and for the present war, and compare the two. The *Journal of Industrial and Engineering Chemistry* is a satisfactory source.

4. With your present laboratory and working space in mind, prepare a sketch showing the most efficient and neatest arrangement of the general materials you require for chemical work in the space assigned to you. After that, use this arrangement habitually. Include also the location of apparatus for general use.

5. Make a topical outline of the contents of this chapter. Doing this is good practice and will be useful in review.

6. This is an introductory chapter designed to give you a working preview of explosives chemistry. What information which you did not know from your previous chemical training did you acquire? What aspects not mentioned here are you familiar with?

7. What are the required precisions for various types of chemical work—commercial, laboratory, research? What are the general types of precautions for different instruments and what procedures are necessary to attain them?

8. Report on the history of the explosives industry in the United States.

CHAPTER 2

The Nature of Explosives

Explosion. Explosion is a familiar phenomenon which we identify as a sudden event which is accompanied by a loud *noise* or report, more or less *flame*, and the *shattering* of nearby material into fragments which are hurled away from the explosion center at high velocities. An explosive is probably most easily defined, with substantially equal accuracy, as a material which under some circumstances will behave explosively as just stated, as in any other way. The list of accompanying phenomena can be made somewhat longer and they can be more carefully analyzed with respect to their characteristics, but the definition is perhaps more meaningful than any other that could be made at this point.

The definition is very broad and might include many things not now regarded as explosives because the conditions under which they behave explosively have not yet been called to our attention. Ammonium nitrate, NH_4NO_3, which is rather difficult to explode, has for precisely that reason come to be regarded as an explosive only in recent years. The definition is also practically valuable because any material which can behave in the way described under easily producible or common circumstances possesses elements of danger for those in its presence. Legal classification of explosive materials and rules for their manufacture, handling, and storage are based upon such considerations.

The essential requirements for explosion are, then: (1) a chemical material intrinsically possessing the capacity for a certain behavior, and (2) conditions which initiate such behavior. The necessary conditions usually mean a suitable impulse of some kind. Hundreds of chemical materials which meet these two requirements are known; and doubtless many are still unknown. In those unknown cases, it may be questioned that the order of magnitude of their effects could greatly differ from those now known. Among the chemical substances and classes of substances which are designated as explosives may be included: many simple nitrogen compounds such as nitrogen iodide (NI_3), nitrogen chloride (NCl_3), nitrogen sulphide (N_2S_3), cyanogen (C_2N_2), and chlorazide (ClN_3); hydrazoic acid and its salts, especially of copper, silver, and lead; similarly for fulminic acid, hydrocyanic acid, thiocyanic acid, oxalic acid, picric acid, styphnic acid, and other acids falling into other chemical groups mentioned here; some hydrides as phosphine (PH_3), stibine (SbH_3), and acetylene (C_2H_2), as well as acetylides such as copper acetylide (Cu_2C_2) and phosphides; chlorates and other haloxy salts and compounds; permanganates; many other oxidizing agents such as hydrogen peroxide (H_2O_2); nitrate esters; nitro compounds in both the aliphatic and the aromatic series; diazonium compounds; many organometallic compounds; some ozonides; and in general any mixture of an easily oxidizable substance with a good oxidizing agent.

The familiar impulses which initiate explosive reaction are the application of some kind of energy, typically heat or mechanical shock. Of all the accompanying phenomena, the most significant is the sudden rise in pressure which persists until the reaction is complete; the magnitude of this pressure rise is associated with the amount of heat evolved by the explosive reaction.

Other Definitions of Explosives. An explosive has also been defined as "a substance which, when subjected to heat, friction, percussion, or other suitable initial impulse, undergoes a very rapid chemical transformation, forming other substances, mainly or entirely gaseous, which at the moment of their formation tend to occupy a volume very much greater than that of the original substance."[1] In general we might say that an explosive is any material which will undergo a rapid change accompanied by a large increase in volume. This increase in volume accounts for the pressure, and the heat liberated still further increases the volume of gases formed, usually in a ratio of more than 1,000 to 1. The force produced by the volume increase plus the explosion wave resulting from the rapid compression of the surrounding medium immediately followed by a rarefaction [illegible] account for many of the practical phenomena.

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[1] U. S. A., TM 4–205 (1940), *Coast Artillery Ammunition*, p. 5.

Practically useful explosives, for the most part, are solid initially and change partly or entirely into gases as the result of explosion. Important exceptions are the explosive gas mixtures which furnish power in internal-combustion engines. Single-gas explosives are known, such as chlorine dioxide (ClO_2), chlorazide (ClN_3), acetylene (C_2H_2), and others listed before. Liquid explosives include nitroglycerine and many liquid nitrate esters and nitro compounds. The reactions involved are usually over-all exothermic; and the liberated heat raises the generated gases to a higher temperature, thus greatly increasing their volume and contributing largely to the total force of the explosion.

Berthelot[2] gives eight chemical classes of explosive materials. Of these, for our purposes, the most important are: (1) explosive inorganic compounds such as azides and fulminates; (2) explosive organic compounds such as nitroglycerine and trinitrotoluene; (3) mixtures of oxidizable and oxidizing substances which yield gases on reaction, such as gunpowder, phosphorus and chlorates, sugar and chlorates or perchlorates. He classifies explosives also by physical state—solid, liquid or gas.

For purposes of controlling by law the manufacturing, handling, storage, and transportation, a familiar explosives classification is: (1) low or propellent explosives;[3] (2) high explosives, also known as *brisant* explosives;[4] (3) initiators; (4) pyrotechnic mixtures (which strictly are not explosives ordinarily, although they require care in handling and storage) used for producing smokes and smoke screens, flares, and as incendiary materials. Gunpowder and smokeless powder are examples of propellants, T.N.T. and nitroglycerine of high explosives, and fulminates of initiators. Quantitatively the first two are the important classes.

But the latter classification is based largely on behavior under relatively fixed conditions. It offers no sharp distinction related to chemical composition, and the behavior is dependent upon a variety of factors. The principal differences inherent in the classification are: the rate of explosion, which for some hundreds of pounds of material may be as long as a quarter of a second for a low explosive and practically instantaneous for a high explosive, and (2) sensitivity. But smokeless powder, which is classified as a propellant, is chiefly nitrocellulose, which when detonated is a high explosve; and nitroglycerine, which is classified as a high explosive and is indeed a very sensitive material, merely burns without detonation when ignited by a small flame under proper conditions. The original problem of making nitrocellulose available as a propellant was that of reducing its velocity of explosion to a smaller value.

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[2] Berthelot, *sur la force de la poudre et des matières explosives.*

[3] Sometimes abbreviated, L.E.

[4] Sometimes abbreviated, H.E.

The explosion of a high explosive is characterized as "detonation." Its high velocity of explosion, as compared with a low explosive, produces a shattering effect which is qualitatively different, and makes it unsuitable for driving a projectile. The effect is sometimes compared to a blow as opposed to a push. The rate at which the explosive reaction travels through a high explosive depends on several factors and may vary from 1,000 to 10,000 meters per second. It is the shattering effect which earns the name *brisant* explosive, and makes it suitable for some purposes—as for some types of blasting, initiators, boosters, and bursting charges. Initiators are essentially sensitive high explosives, while the low explosive is useful as a propellent charge for projectiles, although gunpowder, while still important, has since 1888 been largely displaced as a practical propellant.

Experiment. *This work should be done behind a barricade!* (a) Place about 1 gram of gunpowder on an asbestos plate and ignite by a flame from a gas burner. Stand a grain of smokeless powder (**Caution!** As a safety precaution it is well to use for this experiment, a grain of straight nitrocellulose powder not larger than the size for 6-inch caliber, and of the usual multiperforated type.) on the cool plate and ignite the upper edge with a flame. The type of burning which results is known as "deflagration"; it usually indicates potential explosive capacity, and is characteristic of the low explosive.

(b) Crease a piece of paper, then lay it flat on a safe surface, the crease down like a book open for reading. Place 0.5 gram of powdered picric acid on this sheet of paper and about the same quantity of PbO about 2 inches away from it on the other side of the center crease. Put a tin sand bath on a ring stand so that a lighted burner will throw the flame on the underside. Grasp the paper by the ends so that the powders run together and allow them to flow along the crease into a heap on the sand bath. Push a lighted burner under the sand bath and quickly step 10 feet away. Lead picrate, here, detonates with a loud noise, and denting or perforation of the dish. This behavior is characteristic of the high explosive. After becoming familiar with this experiment it may be done more spectacularly with slightly larger quantities. A barricade may be used.

Important Characteristics of Explosives. Up to this point we have been indicating essentially, and not too precisely, a number of the characteristics of explosives, and we may now specify some of them toward which attention should be first directed:

(1) The nature of the chemical change for the material in question, usually expressed by a chemical equation.

(2) The heat of reaction for conventional weights of materials.

(3) The amount and type of energy required to initiate the reaction, which measures the sensitivity of the explosive.

(4) The maximum temperature developed by the reaction.

(5) The speed of the reaction, which may be expressed as the rate of burning of the material or the velocity of propagation of explosion through the explosive.

(6) The relative power of the explosive which may be—not too accurately—stated by the specific pressure, a number of conventional expressions, and the results of a variety of accepted methods of experimental testing.

In the course of the more careful consideration of these very fundamental characteristics other important properties will come to light; such as effects of physical state and density, properties of reaction products, such as their specific heats, and toxicity, and others.

Explosive Chemical Changes. Explosion, as is seen on consideration, is essentially a concatenation of physical phenomena,[5] and so it may not be possible to write a chemical reaction. Thus liquid carbon dioxide (CO_2), suddenly heated by an electric unit or by a chemical combustion mixture, will produce an explosion as the result of sudden conversion to gas; and any liquid gas suddenly heated above its critical temperature in a closed weak container will explode.

Most practical explosives produce the necessary physical phenomena as the result of a chemical change, and for them stoichiometrical relations can always be established to some degree. Thus nitroglycerine explodes:

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[5] The significance of this remark is given further emphasis by consideration of the phenomenon of implosion, which is the reverse of explosion. If a suitable ordinary tin or tinplated container or can be partly filled with water, boiled to expel the air, stoppered quickly, and cooled rapidly, it collapses or implodes from atmospheric pressure. Thermometers lowered to great depths in the ocean in weak containers are imploded into small fragments or a fine powder when the container yields to the pressure of the water.

$$4\ C_3H_5(NO_3)_3 \rightleftharpoons 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

A given explosive may, however, sometimes follow several alternative paths. Nitrocellulose, of 13.2% nitrogen, at differing loading densities may behave variously as follows, accepting the arbitrary formula $C_{24}H_{29}(NO_3)_{11}O_9$:

(a) $4\ C_{24}H_{29}(NO_3)_{11}O_9 \neq 30\ CO_2 + 71\ CO + 41\ H_2 + CH_4 + 35\ H_2O + 22\ N_2$

(b) $4\ C_{24}H_{29}(NO_3)_{11}O_9 \neq 35\ CO_2 + 67\ CO + 39\ H_2 + 3\ CH_4 + 34\ H_2O + 22\ N_2$

(c) $4\ C_{24}H_{29}(NO_3)_{11}O_9 \neq 47\ CO_2 + 57\ CO + 29\ H_2 + 13\ CH_4 + 32\ H_2O + 22\ N_2$

(d) $4\ C_{24}H_{29}(NO_3)_{11}O_9 \neq 63\ CO_2 + 42\ CO + 16\ H_2 + 20\ CH_4 + 37\ H_2O + 22\ N_2$

These equations give merely the volume composition of the resulting gases at increasing loading densities from 0.05 to 0.5. This type of behavior is especially characteristic of explosives having an *oxygen deficiency* (see page 100), but is true to some extent of any explosive. Because of the nature of most explosives, carbon monoxide, (CO), oxides of nitrogen, and other toxic products are always present and under adverse conditions the fumes of explosives may be dangerous, especially in confined spaces. In practice, even where a proper explosive for the job is chosen, overcharging, undercharging, use of an improper detonator, failure to detonate due to deterioration of the explosive or to bad conditions, improper loading, and other conditions may cause excessive fumes. On the other hand, an explosive like trinitrochlorbenzene [$C_6H_2Cl(NO_2)_3$], which normally explodes to produce phosgene ($COCl_2$), has interesting possibilities for military purposes for certain types of bombs and shells. In this field some new types of explosives are clearly indicated.

Heat of Explosion (*Qv*) Most explosive reactions are exothermic over-all. The heat evolved is of importance in determining whether the substances will behave explosively, and in fixing the power of the explosive. Thus all of the heavy metal oxalates will decompose:

$$RC_2O_4 \rightleftharpoons R + 2\ CO_2 + Q$$

ZnC_2O_4, PbC_2O_4, and CuC_2O_4, where $Q = -49.1, -16.7$, and $+5.9$ Calories,[6] respectively, are not explosives, but HgC_2O_4 and $Ag_2C_2O_4$, where $Q = +17.3$ and $+29.5$, are.

For an explosive compound the heat of explosion may be measured experimentally or, as will be seen later, calculated theoretically. In general it will obviously be the difference between the heat of formation of the products of the reaction and the heat of formation of the explosive substance based on the equation weights.

Experiment. The heat of explosion for an explosive (see Chapter 16) may be determined in the usual type of bomb calorimeter just as for foods or fuels. It must be borne in mind that the heat thus determined is at *constant pressure* and the water obtained as a final product in the experiment is a liquid.

In the explosion of an explosive, the reaction is conceived to be a conversion of the explosive into products, some or all gaseous, which instantaneously occupy the same volume as the explosive itself. The significant heat of explosion is, therefore, the heat at *constant volume*, a concept which is to a degree confirmed by stroboscopic photographs. The result of explosion is the production of high explosion temperatures at which water (and sometimes other substances) is a gas.

Explosive compounds may be endothermic as is the case with acetylene, cyanogen, and mercuric fulminate [$Hg(ONC)_2$], which have negative heats of formation; or exothermic, which is the more common case, and includes the more usual explosive materials as nitroglycerine, nitrocotton, T.N.T., picrates, and the like.

The heat of explosion of different explosives varies over the range shown in Table 4. The heats given are in large calories for 1 kilogram of explosive at constant volume with water gaseous. The heat of explosion is a measure of the maximum capacity of the explosive for doing work. Other factors enter into the practical situation, so too much weight should not be attached to conclusions based on them alone.

It is interesting to compare the heat of combustion of ordinary fuels. As a source of energy, explosives are both poor and expensive. Their value lies entirely in the rapid rate at which they produce their energy.

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[6] Unless otherwise stated, calorie measurements in this book refer to kilogram-calories.

Sensitivity of Explosives. An explosive is a system which has the latent capacity to undergo a certain type of reaction which will not manifest itself unless the system is disturbed. The required disturbance is the application of some form of energy—in general, any kind. Thus a mixture of hydrogen and chlorine in a suitable container explodes when exposed to sunlight or ultraviolet light. (This is a simple experiment—try it.) The practical methods of initiating explosive action are by the application of heat from a flame, friction, or electricity; by the use of the mechanical energy of a blow, called percussion; or by detonation which is essentially the use of the somewhat more powerful blow furnished by the explosion of another explosive. The amount of energy required is a measure of the sensitivity of the explosive and different explosives vary widely.

TABLE 4

SOME HEATS OF EXPLOSION

Explosive	Q_v in Calories per kilogram
Black powder	501
Nitroglycerine	1,526
Nitrocotton (N = 13%)	1,100
T.N.T.	656
Picric acid	847
NH_4NO_3	384
Dynamite 40%	1,290
$Hg(ONC)_2$	420

SOME HEATS OF COMBUSTION

Fuel	H in Calories per kilogram
Petroleum	11,000
Coal	8,000
Wood	5,000

Experiment. *Estimation of Temperature of Ignition.* (**Caution!** Do not use this test for initiators. Both experiments should be performed behind a barricade.) (1) Place 0.1 gram of the desired explosive in a test tube loosely stoppered and heat it in a suitable bath, raising the temperature at the rate of 5°C. per minute. Record the temperature at which ignition or explosion occurs.

(2) Set up a Wood's metal bath, heated by a gas flame. Put 0.1 gram of the explosive in an empty copper blasting-cap shell and place it with the closed end down in the bath. Heat the bath to raise its temperature

5°C. per minute until ignition or explosion occurs and record the temperature. This test may also be conducted by preparing a series of shells and inserting them one at a time as the bath temperature is raised by 5°C. steps.

TABLE 5

EXPLOSION POINT

(These figures were obtained by the procedure of the accompanying experiment. They vary widely with the conditions of determination.)

Explosive	Explosion point, °C.
Black powder	> 225
Nitrocellulose (13% N)	185
Nitroglycerine	160
Picric acid	> 225
Nitrostarch	170
$Hg(ONC)_2$	160
NH_4NO_3	> 225

Various other similar tests are used. Table 5 shows the explosion points of a few explosives, but these values vary often by as much as 20° or more, and very powerful explosives often merely deflagrate on heating.

Experiment. *Estimation of Sensitivity to Percussion.* (**Caution!** Use a barricade.) Many explosives are exceedingly sensitive to shock. Let us test nitrogen iodide (NI_3). Add solid iodine crystals to 15 cc. of concentrated NH_4OH. Stop when a brown precipitate is formed in an amount which seems sufficient to be filtrable. (This precaution is very important the first time one makes NI_3, as the substance is violently explosive and one should not have it in any quantity until he has had some experience with its behavior.)

$$4\,NH_4OH + 6\,I \rightleftharpoons 3\,NH_4I + 4\,H_2O + \downarrow NI_3$$

The actual compound is probably a double salt, NH_3NI_3.

Filter and wash the precipitate first with alcohol and then with ether. NI_3 may be kept under alcohol or ether, the latter being more convenient. Explosives are often very much less sensitive when wet with an appropriate liquid. Water may often be used. Wetting is a convenient safety method for storage of sensitive explosives.

Open out the filter paper on an asbestos board and allow it to dry in air. When dry, touch it lightly with the far end of a long pointer (use extreme care!) or even direct a puff of air upon it. It explodes violently. NI_3 is a very sensitive explosive, far too sensitive for practical use, as it is too dangerous to handle. It should never be kept in a dry state.

A practical test of shock sensitivity is to fire a bullet from a gun into the explosive from short distances. Such a test is practically important for all military explosives. T.N.T. will withstand the shock of impact of an army-rifle bullet without explosion.

A usual laboratory test of shock sensitivity is to drop a known weight (usually 2 kilograms) upon the explosive and measure the length of fall necessary to cause explosion. Figure 2 shows a convenient apparatus. The 2-kilogram weight runs on two smooth guides and the distance of fall is read on a meter stick mounted alongside. The bottom of the apparatus is essentially an iron anvil (but note the cup for holding the explosive) and the explosive is squeezed against it by the plunger which receives the blow of the falling weight. In performing an experiment, a weight of the explosive, either 0.1 gram or enough to give an easily audible explosion, is wrapped in tinfoil and placed in the cup below the plunger, which is then put into place.

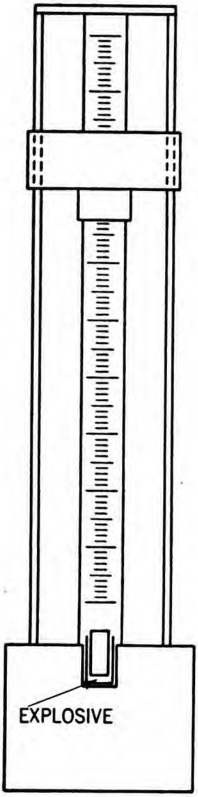


FIGURE 2
Drop-Weight Sensitivity Apparatus

Experiment. *To Determine the Shock Sensitivity of an Explosive.* Employ the apparatus shown in Figure 2. Wrap 0.1 gram of explosive like a wafer in tinfoil. Drop the weight upon it at different heights until explosion occurs, and then use more or less as determined by the audibility of the explosion.

After selecting an appropriate specimen, make up in tinfoil a number of samples as nearly alike as possible. Test a specimen with 2-, 5-, and 10-centimeter falls, and then at 20-centimeter intervals until explosion occurs. Then work back using half the distance between the point of explosion and no explosion until a contradictory result is obtained.

Using the shorter distance, test five samples and report the results. If more than two samples fail to explode repeat the test with five samples at the upper figure.

Table 6 gives a set of results for explosives in such a test. These results also vary considerably for different specimens, depending on physical state and other factors, and of course, for all mixture explosives such properties are largely dependent upon degree of incorporation. Since mechanical shock is always present in handling and transportation, this test is very useful. Any explosive for which shock sensitivity according to this test, using a 2-kilogram weight, is below 10 centimeters is highly sensitive and dangerous to handle. This distinction includes the detonators, which also usually detonate on ignition. For explosives with drop sensitivities between 10 and 25 centimeters there is danger of explosion in handling, but care will minimize it; if shock sensitivities measure between 25 and 100 centimeters, explosion in handling is possible but not likely with any reasonable care; and if they measure above 100 centimeters such explosion is almost impossible. However, the presence of sharp gritty material in an explosive—such as sand, glass, or metal particles—greatly increases its shock sensitivity. This increase is possibly due to concentrating compression forces at the points of the hard particles; and such impurities must be scrupulously avoided in manufacturing processes.

TABLE 6

SHOCK-SENSITIVITY TEST—DROP DISTANCE FOR 2-KILOGRAM WEIGHT

Explosive	Drop distance centimeters
$Hg(ONC)_2$	2
Nitroglycerine	4
Lead picrate	5
Guhr dynamite	7
Blasting gelatin	12
Gelatin dynamite	17
Smokeless powder	30–54
Picric acid	35–95
Zinc picrate	60
T.N.T.	57–90
Black powder	85–100
Dinitrobenzene	120
Nitrocotton + > 20% H_2O	> 180
NH_4NO_3	> 180

The result of this impact test is often expressed in terms of the number of kilogram-meters of energy (or other units of mechanical work) necessary to cause explosion. However, there is no direct correspondence between the amount of mechanical energy required and the temperature of ignition. Such direct correspondence would not, of course, be expected since they are different kinds of units, but there are some complex theoretic relationships. $Hg(ONC)_2$ is more sensitive to shock than $Ag_2C_2O_4$, but in the ignition test, according to A. L. Kibler, $Ag_2C_2O_4$ explodes before $Hg(ONC)_2$.

Explosives become more sensitive to shock with rising temperature, and substances which do not function as explosives at ordinary temperatures may do so at higher temperatures, for example potassium chlorate, $KClO_3$.

Experiment. *Temperature and Shock Sensitivity.* Draw out a glass rod to the thickness of heavy wire for about an inch at one end, and dip that end into molten $KClO_3$ until a fairly thick coating has been obtained. Fit a cork on the upper end so that it will hold the rod in the center of a 1-inch test tube with the tip about 10 millimeters from the bottom. Now mount the test tube on a stand in a vertical position so that it is heated to redness for about 2 inches from the bottom up. When red, insert the rod. The potassium chlorate melts and drips into the hot bottom of the test tube where each drop explodes as it lands. Potassium chlorate is a serious hazard in a fire.

Many materials explode when dropped on red-hot metal plates and this, too, is a familiar test.

Initiation by Detonation. We shall not discuss the relative power of explosives at this point, nor experimental methods of determining it. The fact is, however, that many powerful explosives do not explode at all by either ignition or impact, and that others which thus do explode develop very low power by these methods. But if near these explosives small amounts of other explosives are exploded (the two types do not actually have to be in contact) the insensitive explosives explode at once and with great power. This phenomenon, known as initiation by detonation or sympathetic detonation, is one of the discoveries of Alfred Nobel; and is very useful, since all high explosives in practice are fired in this way. The explosives used for such purposes, which are usually more sensitive, are known as initiators, and the devices in which they are used as detonators, but the two terms are often employed in the same sense.

A certain minimal amount of an initiator is required to explode another explosive, and for the same explosive this amount will differ for different initiators. Thus 0.3 gram of $Hg(ONC)_2$ will detonate guncotton, but the same explosive requires more than 6.5 grams of NI_3. Full power of the explosive is not developed at the threshold of initiation. The amount of the initiator varies with the amount of the main charge and in practice the amount and nature of the initiator is usually determined by careful experiment. In practice the initiators usually employed are $Hg(ONC)_2$ and $Pb(N_3)_2$. Commercial blasting caps are detonators which formerly contained fulminate-chlorate mixture; other mixtures are in current use (see page 332). They were made in graduated sizes, a No. 1 cap containing 0.3 gram of the mixture and a No. 6, which was the commonly used size, 1 gram. In the United States today, nothing smaller than No. 6 is ordinarily made, and blasting-cap initiators usually have a different composition. In detonating nitroglycerine it was found that a No. 1 cap developed only 32% of the *brisant* power of 10 grams of nitroglycerine, but 71% for nitroglycol and 84% for methyl nitrate. A No. 6 cap developed 78% for nitroglycerine, and a No. 8, 100%. For commercial use it is wise to use the larger caps. For military purposes, wherever the size of the charge would require such large amounts of the sensitive initiator for efficient firing as would make the device dangerous to handle, it is customary to reduce the amount of the initiator and use it to fire an intermediate explosive, known as a "booster," which then fires the main charge. Tetryl is commonly used as a booster.

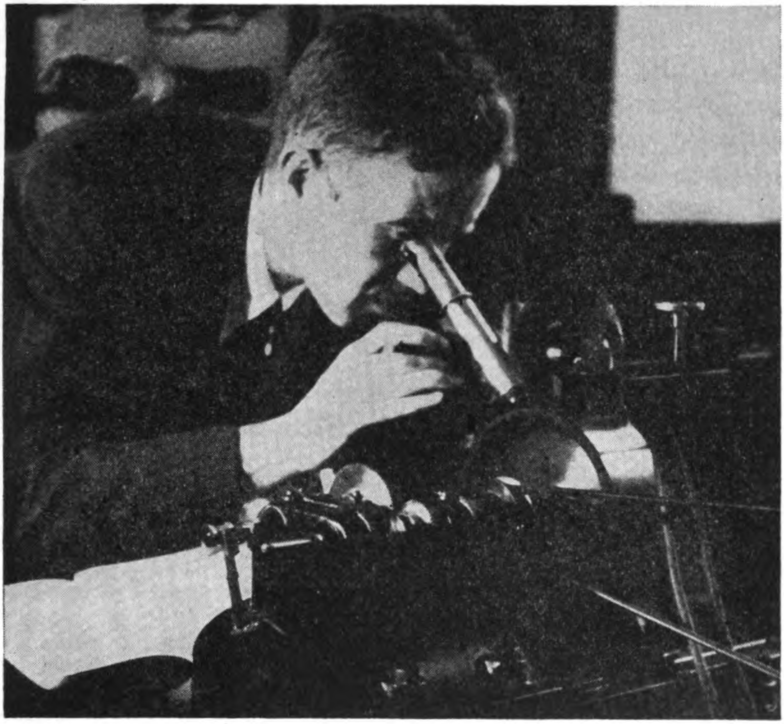
There have been various theories of initiator action. One was that the explosion wave of the initiator synchronized with some vibration peculiar to the explosive in a kind of sympathetic vibration. One obvious conclusion of this theory would be that the best initiator for an explosive would be the same explosive, but this deduction is by no means always true. Today it is usually considered that while the explosion wave does initiate and will act at a distance, it is rather because of its energy content, and initiation by detonation is merely a more powerful variety of percussion. While it is true that the initiator does not have to be actually in contact and under exceptional conditions its effect may be propagated over distances of several feet or more, in commercial practice it is well to have either actual contact or else separation of only a fraction of an inch to be sure of positive detonation. In small separations, however, the interposition of other substances as glass, metal, or paper does not interfere seriously in practice.

Beyond the tests and discussions already presented it may be said that the sensitivity of explosives is a distinctly variable phenomenon influenced by many factors, among which should be emphasized the physical state of the explosive, as well as its physical form—granular, flake, loose powder, cast solid, and the like. Massive solid is usually less sensitive than the granular form. Many physical properties affect sensitivity—viscosity, density, hardness; nature of surface in contact (iron and steel tools are to be avoided in explosive handling, in favor of copper, lead, or wood also because of possible sparks). Excessive compression, in general, diminishes sensitivity; for example, $Hg(ONC)_2$ compressed by slowly applied pressures over 3,000 pounds per square inch becomes less sensitive and above 20,000 will not detonate by percussion or ignition with certainty. The presence of impurities influences sensitivity. Substances which tend to soften explosives diminish sensitivity when mixed with them—as for example, vaseline and fatty oils. On the other hand, many impurities, whose effects are usually specific, may greatly increase sensitivity. Explosives are essentially unstable systems and tend to undergo decomposition with age, often with a marked increase in sensitivity, although this is less true for the nitro explosives in general than for the nitrate esters.

Velocity of Explosion. It is clear on consideration that in general, when an explosive reaction is initiated in a mass of explosive, it starts in a localized region and must then propagate itself throughout the mass. The rate at which this is accomplished is known as the velocity of detonation.

Earlier methods of measuring velocity of detonation consisted in preparing a long cylindrical column of explosive, firing it at one end, and measuring the time it took for the explosion to travel between two points along the length of the column, a measured distance apart. The time is, of course, very short and its measurement is a matter of some difficulty. A Le Boulengé chronograph has been employed. The method is still used for determining absolute velocities with a Mettegang recorder. This device consists of a steel cylinder with a smoked surface, carefully mounted so that it can be rapidly rotated at a known and regular speed. Fixed so that its point nearly touches the drum is a platinum wire which is part of an electric circuit so designed that when it is broken a spark passes between the platinum point and the drum, which is thus clearly marked. The two fixed points on the explosive are wrapped with thin copper wires, each of which is part of a circuit. They are successively broken by the explosion, thus marking the drum at two points whose distance apart, when carefully measured, permits the time to be computed.

Dautriche[7] invented a method for determining relative velocities of detonation, Figure 3. *A* is the cylindrical piece of explosive whose velocity of detonation is to be measured. *B* is a standard explosive in the form of a thin cord (about 6 feet of Cordeau-Bickford) which is inserted in or wrapped around explosive *A* at two points, *P* and *P′*, a known distance, *D*, apart. *C* is a lead plate 18 inches by 3 inches by $\frac{1}{4}$ inch, on which a scratch is made to indicate the exact midpoint of *B*



Mettegang Recorder

This precision measuring instrument is used to check the rate of detonation of explosives. It can measure accurately a millionth of a second. By the use of this apparatus it is possible to maintain a high standard of uniformity and reliability of explosives.
(Courtesy of Hercules Powder Company)

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[7] Dautriche, *Com. Rend.* 143, 641, 1906.

(P'') and B must rest on C approximately as shown. If A is now detonated by the detonator, its explosion wave will start to travel and will first initiate explosion in B at P which will travel along B from right to left, and then a little later at P' which will travel along B from left to right. The two waves in B will meet at some point which, if on the lead plate, will mark it by a deeper furrow than at other points (Munroe effect), P'''. Now:

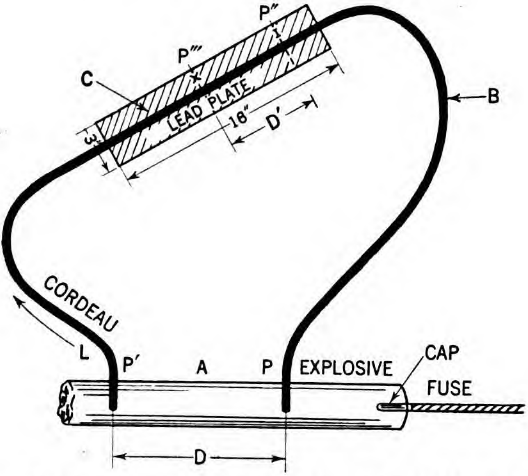

FIGURE 3: **Dautriche Method for Measuring Rate of Detonation**
(Reproduced by permission of Ensign-Bickford Co.)

Let L = total length of B, which does not have to be measured.
V = velocity of detonation of A.
V' = velocity of detonation of B.
D' = distance between P'' and P'''.

Since the two explosion waves must have been traveling the same time in going from P to P''' by different paths,

$$\frac{D}{V} + \frac{\frac{L}{2} - D'}{V'} = \frac{\frac{L}{2} + D'}{V'},$$

therefore

$$\frac{V}{V'} = \frac{1}{2}\frac{D}{D'}.$$

It is evident that this experiment enables one to measure relative explosion velocities, and if one knows V', absolute velocities.

explosion increases with increases in pressure and temperature. This behavior is very marked in the case of explosives with low speeds—gunpowder in the form of a safety fuse burns at the rate of only a few millimeters per second, whereas under the pressure conditions in the powder chamber of a gun, both black powder and smokeless powder burn very much more rapidly. These phenomena have been carefully studied in the case of homogeneous gaseous explosion mixtures.

The effect of excessive compression—that is, of increasing the density of a solid explosive—on the velocity of explosion is noteworthy. At first, with increasing density the rate of explosion increases until it reaches a maximum; then it decreases again. Table 8 gives experimental results for 75% guhr dynamite. The effect is practically useful. Gas mixtures exhibit the phenomenon if they contain inert components.

TABLE 8

VELOCITY OF EXPLOSION

Density	Velocity, meters per second
0.63	1,991
0.79	2,397
0.85	2,563
1.34	3,670
1.54	5,230
1.62	6,794
1.69	4,207
1.71	2,460
1.74	Failure

Given the possession of the other properties requisite for explosion, probably the most determining factor of total behavior is velocity of detonation. The difference between low speeds—below 1,000 meters per second—and high speeds is accompanied by a qualitative difference in effect and power—a heaving effect as opposed to a powerful shattering blow, and is the basis for the classification into low and *brisant* explosives, which, however, is not a chemical classification since it is influenced by other than chemical conditions. Nitrocellulose is usually a low explosive when ignited unconfined, whereas when detonated it is a high explosive.

The velocity of explosion of a given explosive increases as the amount of initiation increases beyond the threshold value, and can be increased in the laboratory to a maximum value by adjusting all other conditions to their optimal values. Practically, however, the best velocity obtainable in the usual commercial form is more significant; for example, as manufactured in paper cartridges. A high velocity of explosion is the outstanding factor in the choice of an efficient initiator, sensitivity and other factors being satisfactory, and this is one reason why P.E.T.N. is coming into use for this purpose.

Mechanism of Explosive Reactions. In the nineteenth century, explosive systems were considered to be chemical systems possessing an inherent structural weakness and high energy content, in an essentially metastable condition. They were often likened to a cone standing on its apex. In the prediction of their phenomena, such as sensitivity and power, almost complete reliance was placed on the thermochemical data; and the effort was made to elucidate their action in terms of structural chemical relationships, much as has been done for color and chemotherapeutic value.

While these concepts have some validity in certain cases and in aspects of all cases, modern physicochemical considerations and experiments indicate that the general problem is much more complicated. One obvious weakness of the early concept is that explosion is basically and essentially a physical phenomenon caused by the simultaneous appearance of certain physical effects.

To be sure, explosions are usually produced in practice by substances which operate by chemical reactions. In mixture explosives, however, the individual substances may have no chemical instability at all in the usual sense. Under the proper conditions, a mixture of liquid oxygen and powdered charcoal, or any carbonaceous dust suspended in air, is violently explosive by chemical reaction. For all mixture explosives, regardless of the chemical stabilities of individual components, the conditions determining behavior will usually be the degree of incorporation of the mixture and related purely physical considerations. Even in the case of single-component explosive substances, the thermochemical data alone give only the most general idea of the explosive capacity. While highly endothermic compounds like acetylene in general have explosive capacity, an exothermic compound like nitroglycerine is often much more sensitive. While heat of explosion indicates in general the maximum work and to some extent the power of an explosive, heat of explosion is not, as we have seen and shall see, an exact measure of practical performance in many ways.

On the other hand, the presence of certain chemical linkages can be identified with explosive properties: the peroxide linkage; the O—Cl linkage in chlorates, perchlorates, and hypochlorites; nitrogen-halide linkages in some compounds; N=O in nitrites, nitrates, organic and inorganic, and nitro derivatives; N=N in diazo compounds and hydrazoic acid; N≡C in cyanogen and fulminates; C≡C in acetylene and its homologues; and others. Bayer's strain theory and modern conceptions of electronic structure give excellent pictures of the internal strain present in such molecules. Such structures unquestionably possess an inherent metastability and, therefore, a tendency to reaction to a more stable configuration, which will occur when the required energy of activation is supplied to them.

In terms of a modern viewpoint, explosive reactions are simply one type of chemical reaction which is to be accounted for by the general explanation of the mechanism of chemical reaction. The explosive characteristics are largely related to the fact that such reactions, being exenergetic along with other properties, are self-accelerating, but here as elsewhere it is the energy which accelerates the chemical reaction. The classic methods of measuring the sensitivity of explosives are merely crude and sometimes incorrect ways of estimating the energy of activation for the specific reaction involved. The situation is further complicated by the fact, true in general, that the problem of determining the exact mechanism of a heterogeneous reaction still baffles us in the case of reactions apparently much simpler than those of most explosives. Extensive study in the field of homogeneous gas reactions, including those of an explosive nature, has yielded a mass of knowledge for many reactions related to mechanism, energy of activation, velocity, equilibria, and the quantitative variation of these with such other factors as pressure, temperature, catalysis, and concentration. The application of these results at present to the heterogeneous systems presented by most explosives can, at best, be done only qualitatively, but it has already effected a complete change in point of view, and presents a fascinating and fruitful field for further research; while the work already done has been of tremendous practical value in the commercial design of internal-combustion engines, and elsewhere.

Discussion Questions and Exercises

1. Write chemical formulas for 25 compounds, not mentioned specifically in the text, which you would expect to have explosive properties.

2. Tabulate and compare all of the methods of classification of explosives which have been mentioned so far.

3. Describe nitroglycerine in terms of the outline on page 23. See the later text for missing information.

4. Calculate the relative volume of the gaseous products of nitroglycerine explosion at N.T.P., at 100°C., and 3,000°C., referred to that of the liquid at ordinary temperatures.

5. Note the relative changes in percentage compositions of the gases in the explosion of nitrocotton with increasing loading density.

6. Write a possible explosion equation for trinitrochlorbenzene.

7. In general, would you expect endothermic compounds to have explosive properties? Would you expect them to be more sensitive than some other compounds? Why?

8. Compute the drop-weight results in Table 6 in units of mechanical energy (such as kilogram-meters) and in calories.

9. Which would you expect to have the higher velocity of detonation—granular T.N.T. or melted and cast T.N.T.? Which would you expect to be more sensitive? Why?

10. To be reliable within 10%, what unit of time must an instrument for the determination of absolute velocities of detonation be able to record, if the column of explosive is to be not more than 10 ft. long? What physical effects can you think of which might be suitable?

11. In what direction is a blasting cap most effective as a detonator? Why?

12. Consult the first volume and the most recent edition of *Chemical Abstracts* and record two or three problems of research in explosives which occupied attention at those times.

13. What could explosives described as follows be used for? (a) High explosion velocity, very low sensitivity, and high power. (b) High explosion velocity, moderate sensitivity, and high power. (c) Low explosion velocity, moderate sensitivity, and good power. (d) High explosion velocity, 2 centimeters of the 2-kilogram weight, and good power. (e) High explosion velocity, <0.1 centimeter of the 2-kilogram weight, and high power.

14. What is a "chain reaction"? Illustrate. What relation has it to the mechanism of explosion reactions?

15. Write an equation for an explosion reaction which furnishes the power in an internal-combustion engine.

16. With a lead plate, as described on p. 33, what range of speeds may be easily measured with Cordeau-Bickford, $V' = 17{,}500$ ft. per second if D equals six inches?

CHAPTER 3

Black Powder, Pyrotechnics, and Incendiaries

Introductory. Gunpowder, or black powder[1], is essentially a mixture of sulphur, charcoal, and potassium nitrate (niter or saltpeter). Initially the materials were finely ground and the result was literally a powder. After the year 1600 black powder began to be made in grains as the result of empiric observations regarding the rate of burning; and beginning about 1860 General T. J. Rodman made studies of grain size and density and their effect on the rate of explosion, which will be discussed in Chapter 7. His results greatly influenced practice. Since the practical abandonment of gunpowder, about 1888, as a propellent explosive the results are no longer important here, but are elementary considerations for all propellent explosives.

Composition and Reaction. The stoichiometrical equation usually given for the explosion of gunpowder is:

$$2\ KNO_3 + 3\ C + S \rightleftharpoons \uparrow N_2 + \ \uparrow 3\ CO_2 + K_2S$$

The reaction is essentially a relatively slow combustion, which supplies its own oxygen. The yield from this reaction would correspond to a component-weight ratio, in the order given, of approximately 75:15:10 and this ratio is now a usual formula for military powders. In ancient times the tendency was to use less niter and more carbon and sulphur. Today there is some variation in composition, the usual range being from 6:1.2:0.8 to 6:1:1. On explosion a variety of products have been identified in varying amounts, in addition to those given—CO, H_2S, H_2, CH_4, O_2, K_2CO_3, K_2SO_4, K_2S_x, $KCNS$,

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[1] A convenient reference book which gives the formula and alternative names of many explosives is Bebie's *Manual of Explosives, Military Pyrotechnics, and Chemical Warfare Agents* (Macmillan, 1943).

$(NH_4)_2CO_3$ as well as some of the original components, and the amounts are naturally and markedly influenced by the original composition and the conditions of firing. Blasting, propellent, and igniting powders, as well as pyrotechnic mixtures may vary in composition. In general, increase in nitrate content increases the rate of burning. Increase in sulphur content gives a brown powder.

TABLE 9*

ENGLISH POWDERS

Year	Parts, by weight		
	Saltpeter	Charcoal	Sulphur
1250	41.2	29.4	29.4
1350	66.6	22.2	11.1
1560	50.0	33.3	16.6
1647	66.6	16.6	16.6
1670	71.4	14.3	14.3
1742	75.0	12.5	12.5
1781	75.0	15.0	10.0

EUROPEAN POWDERS

Year	Parts, by weight			
	Countries	Saltpeter	Charcoal	Sulphur
1338	France	50.0	25.0	25.0
1560	Sweden	66.6	16.6	16.6
1595	Germany	52.2	26.1	21.7
1608	Denmark	68.3	23.2	8.5
1650	France	75.6	13.6	10.8
1697	Sweden	73.0	17.0	10.0
1882	Germany	78.0	19.0	3.0

* Hime, *Gunpowder and Ammunition.*

A gram of dry black powder yields at N.T.P. from 200 to 300 cc. of gases and from 500 to 800 gram calories of heat. Its explosion temperature (*Te*) is about 2,100°C. (this is also recorded as higher) and its density is about 1.74. Its sensitivity is 70 to 85 centimeters with a 2-kilogram weight.

Gunpowder may be easily destroyed, if desired, by dissolving out the nitrate with water, and the residue is then harmless. The purity and nature of the materials used for the manufacture of gunpowder are important factors in the properties of the product.

Potassium Nitrate, KNO_3. This compound may be purified Bengal saltpeter or it may be manufactured by mixing solutions of sodium nitrate and potassium chloride of the proper concentration while hot. After separating the precipitated sodium chloride, the potassium nitrate separates on cooling, with a little sodium chloride, which may be removed by recrystallization.

The purified product forms white, rhombic crystals melting at 334°C. The solubility in water, which is important in powder manufacture, is 31.6% by weight at 20°C. and 247% by weight at 100°C. Its purity may be tested by nitrogen determination in the nitrometer (see page 232), and the theoretical percentage is N = 13.86%.

Charcoal (*C*). Charcoal is a form of elementary carbon which is the solid residue of the destructive distillation of wood. Any wood might be used, but for gunpowder, dogwood, elder, or preferably willow are desirable. After cutting and stripping of the bark, the wood may be allowed to season for two or three years. It is then heated in properly designed retorts at from 800° to 900°C. for about 7 hours, although 330°C. has recently been determined as an optimum for certain woods. Some volatiles are desirable and overheating will reduce the residual hydrogen and oxygen too far. The charcoal is cooled out of contact with air, then ground and sifted. It should then contain from 1% to 3% of hydrogen, from 8% to 15% of oxygen, and the less ash the better.

Charcoal is a black powder, insoluble in all ordinary solvents, with a specific gravity of about 1.9, and burns on heating in air or oxygen to give carbon dioxide. It may be analyzed for total volatiles (including moisture), for carbon by burning off, and for ash as residue.

Sulphur (*S*). Sulphur is a nonmetallic element which occurs free in nature in volcanic regions. It is produced in Italy by the Sicilian process, more largely in the United States by the Frasch process, also as a by-product in certain metallurgical processes; and it is recovered by several industrial methods. At ordinary temperatures, sulphur is a solid which exhibits several allotropic modifications with somewhat differing properties; the best known varieties are the rhombic, the monoclinic, and several amorphous forms.

For gunpowder, sulphur must be pure and is purified by sublimation. Under those circumstances, or after having been cast, ground and sifted, it consists chiefly of small crystals of rhombic sulphur. It is then a yellow powder with a specific gravity of 2.06 and a melting point of 114.5°C., which is very soluble in carbon bisulphide and soluble in some organic liquids. It may be analyzed for moisture, for sulphur by burning off the sulphur as sulphur dioxide, and for determination of the nonvolatile residue.

Commercial Manufacture of Gunpowder. The procedure as described herein is modified to meet the United States Army specifications of May 13, 1941, current at this writing. The student or worker in the field who desires to keep up to date must secure current United States War Department specifications for all military explosives, as they change from time to time.

Preparation of the mixture. The starting materials are weighed out according to the formula desired, and the sulphur and charcoal are ground together in an iron or steel ball mill. Several methods of mixing have been employed. In the French process, now seldom used, the ground ingredients are mixed in a ball mill in which the cylinder is of wood, and the balls are some of lead and some of lignum vitae. In the dry mixing process the components may be mixed by hand or by mechanical devices. Neither of these is a truly dry process, as in practice some water must be added to prevent explosion.

The wet mixing process is the ordinary one. The sulphur and charcoal mixture is stirred into a saturated solution of potassium nitrate at a temperature of about 130°C. (265°F.). The mass is nearly solid, and is spread on the floor to cool and solidify completely, when the lumps are readily broken up and are ready for incorporation. For a 75:15:10 mix at this point they contain about 23% of water.

Milling. 300 pounds of mixture is put on the bed of each wheel mill. The wheels weigh not less than 8 tons each, have an 18-inch face and rotate at 10 revolutions per minute. The material is incorporated for three hours. Edge runners keep the material worked toward the center of the face of the wheel, and lumps formed during this operation, known as wheel cake or clinker, are broken before pressing.

Pressing. Uniform density of the powder before granulation is required to secure consistent ballistic results. The pressing operation accomplishes this uniformity and is carried out in a horizontal hydraulic press. The press plates in the past have been of ebonite, grounded to remove static charge, and pressures have increased from 400 lb. per square inch. Press plates now are usually of aluminum and employ a pressure of 1,200 pounds per square inch. The press cake produced is about 24 inches square, $\frac{3}{4}$ inch in thickness, and weighs about 25 pounds.

Corning. The press cake is fed between crusher rolls in the corning mill. Four sets of crusher rolls per mill are the usual number and the coarser lumps pass successively through them. Mechanically operated shaking screens separate the dust and coarse grains as the charge moves along.

This operation is the most hazardous in the process and one of the most hazardous of the entire explosives industry. The corning mill is situated in an isolated and barricaded building, and the process is remote-controlled. Employees are not permitted inside the building while the mill is in operation.

The product of the corning mill is material which screening has sorted to size, and "dust," which is a by-product useful for fuse powder and fireworks.

Finishing. The finishing operations may be carried out in a single operation when they require about 8 hours, or individually. The grains are rounded and polished by revolving in a wooden cylinder, and may be dried either by passing warm air through the same cylinder or in separate wooden trays. The grains may be glazed by adding about 1% of graphite at the end of the rounding and polishing process and continuing rotation of the cylinder for about half an hour.

Graphite (*C*). Graphite is another of the allotropic modifications of carbon. Natural graphite is found in Mexico and Ceylon, and it is also produced in the electric furnace by Acheson's process. It is a black, hexagonally crystalline material, with a greasy feel and a density of 2.25. There are government specifications for graphite (and other components) to be used for gunpowder.

Specifications usually require that the moisture content of gunpowder be not more than 0.7%; more moisture lowers the efficiency of the powder; yet gunpowder with less than 1% of moisture tends to be quite hygroscopic. Since glazing with graphite tends to reduce absorption of water, the process is used for all propellent powders and in some other uses of low explosives.

Grading. After finishing, gunpowder is rescreened and separated into grades by grain size. Gunpowder grains may be irregular or may be spheres with a diameter variation desirably less than 5% (see Chapter 7). Grade refers to grain size always, not to quality (see Table 10).

For commercial purposes, in general, coarse and fine grades are frequently C, CC, CCC, F, FF, FFF, FFFF, or simply 2C, 4F, and the like. Government specifications specify numbers 1–6 of grade A powder.

Inspection and Analysis of Gunpowder.[2] Military specifications for black powder require that ingredients shall be of standard quality, that the powder shall be manufactured by the process just described, and that it shall have a composition: KNO_3 74.0%, charcoal 15.6%, sulphur, 10.4%, all ±1.0%. The powder must be free from all such foreign matter as sticks and sand, with specific gravity 1.72 to 1.77, and moisture not greater than 0.70%. Granulation for military grades is indicated in Table 10, with not more than 3% retained on the passer screen (see page 125) and not more than 5% may pass the duster screen. Grade A, Nos. 1, 3, and 4 must be glazed with graphite to a bright black polish and be practically free from dust. Grade A, Nos. 5 and 6 are unglazed. Ash for Nos. 1, 3, and 4 must be not more than 0.80% and for Nos. 5 and 6 not more than 0.60%.

High-grade powders for special purposes have regularly spherical grains with a desirable diameter variation less than 5%. Some powders have $NaNO_3$ substituted for KNO_3. These are much cheaper but also much more hygroscopic, but this drawback is somewhat compensated by glazing. Blasting powders in general have irregularly shaped grains of standard screen sizes, which look much like tiny pebbles in shape. Some powders are also made as large single-perforated cylinders, about 1¼ inch in diameter by 2 inches in length with a ⅜-inch perforation. This form is extensively used for blasting and the amount of it manufactured is increasing. At present more than half of all commercial manufacture is this pellet powder.

Sodium nitrate powders are most largely used for commercial blasting purposes, and potassium nitrate powders for military purposes, but not exclusively so.

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[2] U. S. A. Specifications 50–14–1c. See also same, 50–14–4.

The United States Army inspection procedure for gunpowder is exhaustive. The directions follow, omitting the record keeping details.

Select one representative drum from each batch of 5,000 pounds, but not fewer than 10 drums from the entire lot of packed powder. Present specifications require sampling of 10% but not more than 10 containers. Take approximately 1 pound of powder from each of these selected drums. Place one-quarter of each of these samples in a bottle labeled so that the drum from which each sample was removed can be definitely determined. Put aside the remaining three-fourths to form part of a larger blended sample. Mix all ten of these on a sheet of heavy paper, using a scoop and raising and lowering the edges and corners of the sheet. When the sample is thoroughly mixed, quarter it, and then quarter each part again. Take portions from each sixteenth to give a total of about 1 pound. Place this sample in a properly labeled bottle or metal canister, to be used as the sample representing the lot; perform all acceptance tests upon it. Hold for possible future examination the samples that were taken from each of the 10 drums and placed in individual containers, should the tests on the inspector's blended sample show that the lot fails to meet the requirements.

Test for potassium nitrate (or $NaNO_3$). Weigh into a tared Gooch crucible provided with an asbestos mat, approximately 10 grams of sample. Draw through the crucible by suction about 200 cc. of hot water in successive portions of 10 to 15 cc. each. Test the final portion of water passing through the crucible with an excess of strong sulphuric acid containing a few crystals of diphenylamine until there is no blue color reaction indicating the presence of nitrates. Dry the crucible for four hours at 70°C. and weigh. Compute the loss in weight minus the moisture content, and consider the result as the potassium (or sodium) nitrate content; compute it as a per cent of the powder weight. (It is recognized that this includes any water-soluble portion of the charcoal or sulphur.) To test the purity of the nitrate, add 1 cc. of nitric acid (specific gravity 1.42) to the water extract. Evaporate to dryness and dry at 150°C. Thoroughly mix the residue and test 1 gram for nitrogen content in a nitrometer (see Chapter 11). The nitrogen content of the residue should be (United States government specification) 13.84% ± 0.03.

Test for sulphur. Place the crucible, weighed for loss of water-soluble material, in an extractor (Sohxlet or Wiley) on a water bath, and extract for 1 hour with carbon bisulphide. (The crucible must be carefully arranged in the extractor so that the liquid level does not rise above its top, as it is easy to lose carbon mechanically here.) After extraction, wash the crucible once with alcohol and once with ether, using suction, and dry for one hour at 100°C. The loss in weight of the crucible represents sulphur.

Test for charcoal. Consider the residue in the crucible to be charcoal. Determine its weight by subtracting the original weight of the Gooch crucible from the weight of the crucible and residue.

Test for foreign matter. Visually examine the residue in the Gooch crucible at this point for the presence of sticks, stones, sand, and the like.

Test for ash. Ignite the crucible and the residue from the charcoal test in a muffle furnace or over a burner until all of the carbon is burned off. Cool in a desiccator and weigh. Subtract from this weight the original weight of the Gooch crucible to get the weight of ash.

Test for moisture. Grind in small portions some of the original sample to at least 60-mesh fineness. This grinding should be done with great care and not in a metallic mortar. Weigh about 2 grams into a tared weighing dish or covered watch glass. Dry in an air bath for 4 hours at 70°C. Cover, cool in a desiccator, and weigh. Calculate the loss in weight as the per cent of moisture in the original sample.

For the student doing a laboratory analysis it is interesting to calculate the analytical results to a dry basis and determine the manufacturer's formula.

Test for specific gravity. Transfer a known weight, approximately 10 grams, to a 50-cc. specific-gravity bottle, filled one-half to two-thirds with clean mercury. Displace the remaining air in the bottle with mercury, as follows: attach a piece of heavy rubber tubing about 2 feet long to the bottle. Connect the other end of the tubing to one arm of a **Y** tube. By means of another piece of rubber tubing and a short piece of glass tubing extend the other arm of the **Y** tube to dip into a vessel containing mercury. Connect the stem of the **Y** tube with a suction line. Close the rubber tubing leading to the mercury vessel by means of a pinch clamp. Open the vacuum line and evacuate the specific-gravity bottle. After evacuation, close the suction line by means of a pinch clamp placed close to the specific-gravity bottle. Open the pinch clamp on the tubing leading to the mercury vessel and allow the mercury to flow into the bottle. Repeat this operation until the bottle is filled with mercury. Weigh the bottle containing the powder and mercury at 20°C. ± 0.3°C. Add the weight of the black powder to the weight of the bottle filled only with mercury. Subtract from this total weight the weight of the bottle filled with black powder and mercury. This gives the weight of mercury displaced. Divide this weight by the specific gravity of mercury at 20°/4°C. (13.55) to get the weight of an equal volume of water at 4°C. Divide the weight of powder used by this weight to get the specific gravity of the powder.

$$\text{specific gravity of black powder} = \frac{13.55\,A}{A + B - C}$$

where A = weight of sample, B = weight of bottle with mercury, C = weight of bottle with mercury and sample.

Test for granulation. For military powders, granulation may be determined by the method of Chapter 7. Fineness of the various grades is given in Table 10.

TABLE 10

FINENESS OF VARIOUS GRADES OF BLACK POWDER

Designation, U. S. Army	U. S. standard sieve No.	
	Passer	Duster
Grade A No. 1	4	8
Grade A No. 3	12	16
Grade A No. 4	16	40
Grade A No. 5	40	100
Grade A No. 6	100	140

Packing and Marking. Standard military packing is a metal keg holding 25 pounds, lined with a cloth powder bag. For overseas shipment these kegs are crated two to a crate, and markings are specified. Commercial containers may be canisters of metal for smaller sizes of standard weights and are often red; the army kegs are black. Pellet powder is wrapped in paper cartridges like a dynamite stick and packaged in packing cases.

Uses. Army grades are specified for use as follows:

Grade A, No. 1—All igniting charges; M_1, M_1B_1, M_{21}, M_{22} primers; and saluting charges.

Grade A, No. 3—Special uses.

Grade A, No. 4—Base charges for shrapnel, and fuzes; friction primers, Model 1914; obturating friction primers; M_{23} and M_{25} primers; smokepuff charges; bursting charges for practice bombs; practice loaded projectiles; and some subcaliber shells.

Grade A, Nos. 5 and 6—For pellets for primers and fuzes.

In general, black powder is used for some types of mining operations, special blasting purposes, squibs, primers and fuses, pyrotechnics, and cheap small-arms cartridges, and as an ejector for marine torpedoes. In the laboratory, a conveniently prepared fuse known as "black match" can be made by mixing finely ground black powder to a paste with water, incorporating the paste into a piece of ordinary cord, and drying. About the same result can be attained by soaking the cord in a strong hot solution of KNO_3 and drying. Ordinary filter paper may also be used.

Pyrotechnics. Pyrotechnics is the art and science of making fireworks. Such devices appear to have originated in China; they may antedate the discovery of gunpowder and may be the origin of it. Their manufacture was increasingly well-known in Europe after the Renaissance, and they had great popularity. Kings of France during the sixteenth and seventeenth centuries took great interest and pleasure in court displays for entertainment and spent huge sums upon them. This interest has survived to our own day, but the trend is now to confine fireworks to public ceremonies and discourage their sale to the general public. Apart from the amusement feature, certain items such as rockets, flares, and torpedoes have important utilities in marine, aviation, and railroad signaling, and some have military applications.

Pyrotechnic devices have tended to standardize themselves into more or less familiar types: caps, firecrackers, torpedoes, and bombs are principally noisemakers; stars, rockets, flares, pinwheels, Roman candles, and the like, combine fire, color and motion to produce esthetic effects; mines, fountains, Pharaoh's serpents, sparklers, and many other devices use combinations of these and other phenomena to produce results which amuse some people.

In general they are combinations of chemical mixtures and mechanical ingenuity. Weingart[3] and Davis[4] give practical directions for making them. The chemical mixtures are usually black powder or modified gunpowder for propellent purposes, and incendiary or combustible mixtures to produce fire, with various addenda to produce color, sparks, and smoke as desired. Many of the devices in which they appear are essentially bombs or guns, but are constructed of paper, cardboard, and wood instead of the more rugged metal necessary for more lethal purposes. Incendiary mixtures usually employ a chlorate or perchlorate or nitrate oxidizing agent, a combustible such as sugar, starch, dextrin, or sawdust, and for color metallic salts such as those of barium, strontium, or copper. Sparks can be produced by the addition of particles of metal—iron, aluminum, and antimony as well as others. The great increase in volume of $Hg(CNS)_2$ or $(NH_4)_2Cr_2O_7$ on burning is employed in several devices, and may be readily seen by igniting a conical heap in a suitable base using a piece of cotton soaked in alcohol as a fuse. In general, in making up any formula the mixtures should not be incorporated dry but as a

TABLE 11

FLARE MIXTURES*

Component	Per cent by weight			
	Red flare	Green flare	Blue flare	Railway flare
$KClO_3$	16	26	40	
$Sr(NO_3)_2$	64			60
KNO_3				16
$Ba(NO_3)_2$		53	25	
Sulphur				6
Paris green			25	
Charcoal				5
Red gum	9	14		13
NH_4Cl		7	5	
Sawdust	9			
Lamp black	2			
Stearine			5	

* These are usual formulas. A simple red flare could be only sugar and $Sr(ClO_3)_2$, 1:2 by weight.

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[3], [4] See Bibliography.

slurry with water or alcohol, and the safest practice is to go to a standard reference text for specific directions.

Experiment. Fold a sheet of paper down the middle and then open and put down flat with the crease down, like a book open for reading. Put about 0.5 gram of dry powdered red phosphorus to the right of the crease and 0.5 gram of powdered potassium chlorate 1 inch to the left of the crease. By lifting the ends of the paper, allow them to run together in the crease. Under these conditions they usually explode on contact, but if they fail to do so touch the mixture lightly with a glass rod *at arm's length.* This experiment also can be done with more spectacular results with somewhat larger quantities after you are familiar with the behavior.

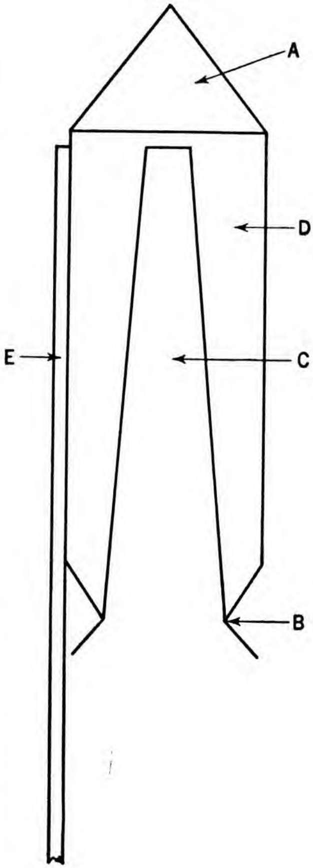


FIGURE 4
The Rocket

Potassium chlorate and phosphorus make a very sensitive explosive mixture used in the fireworks devices known as caps and also, modified, as a percussion mixture in general. It must be made up wet, and when dry explodes on very slight percussion.

Some flare formulas can be found in Table 11.

The noisemakers employ gunpowder under confinement; also silver fulminate which explodes by percussion; and P and $KClO_3$ mixture, which is very dangerous to make and explodes by percussion or fire.

Of all the pyrotechnic devices, perhaps the most interesting is the rocket. It consists (see Figure 4) essentially of a cylinder with a pointed head (*A*) and a constriction (choke) at the tail (*B*). The propelling charge (*D*), (a slow-burning gunpowder can be used) is inserted in such fashion as to leave a tapered conical opening (*C*) in its center which is the first burning surface. It may also have a side stick (*E*) or a tail fin to give it balance in its flight. The fireworks variety may have other pyrotechnic devices included. This description is intended only to illustrate general principles. The propellent force of the rocket is obtained from the recoil effect of the expanding gases of the explosive. The weight of the rocket determines the weight of the charge, but overall efficiency is determined by a variety of factors.

The rocket has important potentialities for aerial navigation and for projectiles; the rocket principle may be used for driving any vehicle. Some pyrotechnic devices use it, pinwheels for example. Its possibilities have not yet received the attention they deserve.

Incendiaries. Incendiary mixtures are designed to produce fire, in general with as high a temperature as may be, and it is desirable that they be difficult to extinguish. While some of them have useful civil applications, notably thermite for welding and familiarly the ordinary match, the principal use of incendiaries is military.

TABLE 12

MATCH MIXTURES

Ordinary match head	Safety match		Scratch mixture; Pair	
P_4S_3	Head	$KClO_3$ or $K_2Cr_2O_7$	$KClO_3$	6
PbO_2		Sb_2S_3	Sb_2S_3	2
Dextrin paste		$CaCO_3$	Glue	1
(Dried and coated with varnish)		Dextrin paste	used with	
		(Varnished)	MnO_2	8
			Red phosphorus	10
	Box	Red phosphorus	Glue	3
		Sb_2S_3		
		Sand		
		Dextrin paste		

The ordinary match head is an incendiary mixture with a kindling temperature sufficiently low that it ignites by the heat of any ordinary friction. The match itself may be impregnated with paraffin, boric acid, and other things to prevent smoldering. In the safety match the incendiary mixture is divided into two parts, one on the head and the other, the "scratch" mixture, on the box; ignition takes place when the two are brought together, although safety matches may be scratched on glass. Another scratch mixture is employed for a similar purpose for fireworks. Some formulas are shown in Table 12.

The magnesium incendiary bomb, also known as the electron and thermite bomb, has wide use as an airplane projectile in modern war. It is essentially a hollow cylinder of cast magnesium with proper ballistic design. The interior contains thermite mixture (Al and either Fe_2O_3 or Fe_3O_4), a fuze with a suitable igniting mixture (powdered magnesium or black powder will do), and may also carry a small high-explosive charge, and the whole in a typical size weighs about 2 pounds (see Figure 5). The fuze ignites the thermite, which ignites the casing itself, and produces temperatures above 2,000°C., and

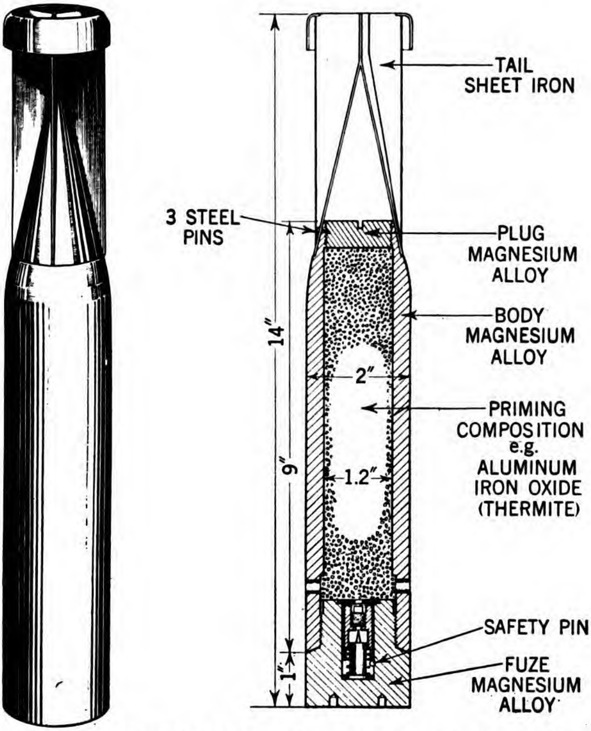


FIGURE 5: **Typical Kilo Magnesium (Electron) Incendiary Bomb**

$$2\ Al + Fe_2O_3 \rightleftharpoons Al_2O_3 + 2\ Fe.$$

The iron melts and

$$2\ Mg + O_2 \rightleftharpoons 2\ MgO.$$

The magnesium combustion may last from 10 to 15 minutes. The burning of the magnesium may be hastened by the use of a spray of water (a stream may cause explosive scattering; this is the subject of some controversy at present), but under any except laboratory conditions such incendiary bombs cannot usually be extinguished because of the great reactivity of magnesium.

Thermite may be used alone in a steel container, as is the Japanese practice.

A convenient practice incendiary bomb of this type for fire-control instruction may be made from scrap magnesium turnings. Wood blocks are made as shown in Figure 6. The space between the inner and outer block is about ½ inch and is packed with magnesium turnings which are pressed after each addition to make them cohere in a dense block. When complete the magnesium cylinder which is hollow should be about 6 inches long and 2 inches in outside diameter. A brown-paper cylinder is put inside, and a single wrapping of thin brown wrapping paper on the outside. Commercial bombs use cardboard containers which burn like a bonfire while the thermite is being used up and this behavior spoils the realism of the effect. The inner cylinder is then packed as shown in Figure 6. The bomb may be fired with a safety fuse tied in place as shown, instead of with a

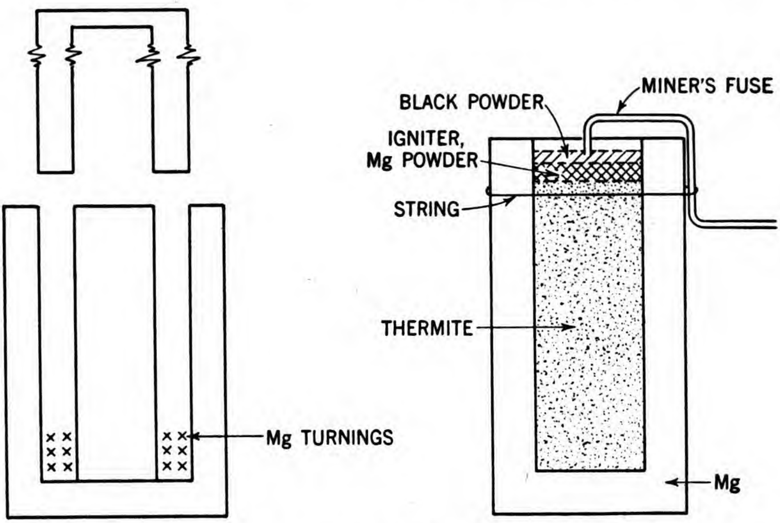


FIGURE 6: ***Left*—Arrangement of Blocks for Packing Magnesium Turnings; *Right*—Practice Incendiary Bomb**

piece of magnesium as is ordinarily done in laboratory experiments. This practice bomb burns about a minute and a half.

In heavy incendiary bombs, which usually weigh upwards of 50 pounds, the combustible may be combined with a high explosive charge to scatter it, and may consist of gasoline or oil. These liquids may be solidified by colloidal jelling, using about 10% of their weight of sodium stearate. Other combustibles may be used, together with a suitable igniting fuze. The effects of these large bombs can not usually be controlled by individual firefighters.

There are numerous other incendiaries. A mixture of sugar with potassium chlorate ($KClO_3$) bursts into a hot lasting flame if a drop of sulphuric acid is applied to it. This mixture is often a convenient igniter for experimental explosive devices. A mixture of ammonium chloride and ammonium nitrate (NH_4NO_3 and NH_4Cl), covered with zinc dust, catches fire and burns hotly with a bright blue flame if moistened with a drop of water . A solution of phosphorus in carbon bisulphide (CS_2) catches fire spontaneously on evaporation in air. This mixture is used to soak cardboard for the so-called visiting-card type of military incendiary; the cards are cheap to make and occasionally useful for surprise. Many organic compounds take fire spontaneously on contact: for example, warm turpentine with chlorine, metallic alkyls such as zinc diethyl [$Zn(C_2H_5)_2$] with air, compounds containing the cacodyl radical [$(CH_3)_2As'$] with air, and related compounds with air.

Other Mixture Explosives of the Gunpowder Type. In general, explosive mixtures of the low-explosive type may be made by substituting chemically similar materials for any of the components of gunpowder, either in part or in whole. Many have been proposed, and some of these have applications. Chlorates and perchlorates may replace potassium nitrate (KNO_3). These mixtures are more sensitive to shock than gunpowder and are therefore more dangerous to handle —the perchlorate mixtures are less sensitive than those of the chlorates—but the sensitivity may be reduced by mixing them with a little oil or other materials to soften the mixture. $NaNO_3$ has been mentioned, and may be purified Chile niter. It is a better oxidizing agent than KNO_3, but is more hygroscopic. Cheap commercial blasting powders contain it, and it may be given better keeping qualities by heavy graphite glazing.

Guanidine nitrate ($NHC(NH_2)_2 \cdot HNO_3$) or KNO_3 and charcoal, without sulphur, will function for some purposes. So will NH_4NO_3 with either charcoal or sulphur, or both, or neither (for example, nitramon)—although NH_4NO_3 alone is a high explosive but a difficult one to detonate. Sodium cresol sulphonate and $NaNO_3$; and ammonium picrate and potassium nitrate have been used.

Smokes and Smoke Screens. A process which yields a dense cloud of smoke, by combustion or otherwise, has utility for many purposes. The materials may be reaction mixtures that produce the cloud of colloid particles we call a smoke, or combustible mixtures with volatile solids which are vaporized by heat. "Choking" an oil fire produces dense clouds of carbon; phosphorus in burning forms a heavy white cloud of P_2O_5. Oleum (see Chapter 9) fumes strongly in moist air—and air, especially at sea, is usually moist enough to produce a dense fog. Ammonia and hydrogen chloride yield dense white clouds of NH_4Cl. This last reaction is the one commonly employed in sky-writing as well as for military smoke screens. Actually $SiCl_4$ or $TiCl_4$ are used with ammonia, moisture in the air causing these reactions:

$$SiCl_4 + 4\ H_2O \rightleftharpoons Si(OH)_4 + 4\ HCl$$

$$HCl + NH_3 \rightleftharpoons NH_4Cl$$

The hydroxide consists of heavy white particles which function as a stabilizer for the otherwise light and readily dispersible NH_4Cl. Colored smokes may be made by incorporating a combustible mixture the heat of which will volatilize an included colored material. Dyes such as paranitraniline red, auramine, chrysoidine, indigo, rhodamine red, malachite green, methylene blue, and paranitraniline yellow may be used.

Discussion Questions and Exercises

1. Prepare a "flow sheet" for the commercial production of gunpowder. Consult some of those given later in the text, if necessary. In the future do this for all explosives whose manufacture is described, if it is not given.

2. Write equations for the explosions of gunpowder which would account for the formations of some of the products formed in smaller quantities. From a consideration of these equations, can you see any factors, such as composition and loading density, which would tend to produce them?

3. Secure government specifications for KNO_3, S, graphite, and charcoal, and tabulate requirements. (U. S. A. Specifications 50–11–26, 50–11–40, 50–11–41, 50–11–42.)

4. Review the usual commercial processes for the production of the components of ordinary gunpowder.

5. Describe the effect of increasing amounts of internal water on the explosion of gunpowder.

6. Determine the raw-material cost of producing 2,000 pounds of gunpowder.

7. Estimate the time required to finish a batch of gunpowder.

8. Tabulate the analytical results of five of your classmates for a complete analysis of gunpowder by the method given and where you note excessive deviations from the average try to establish the cause.

9. What is the chemistry of the diphenylamine test on page 46?

10. What other methods of determining specific gravity are there? Would any of them be applicable to gunpowder?

11. If laboratory time permits, get specific directions, and make up and use one pyrotechnic or incendiary mixture.

12. Report on some of the approved methods of extinguishing magnesium incendiary bombs, including materials used such as water, sand, salt, powdered pitch, mixtures of the last three, powdered cement, and types of equipment. Why would chemical fire extinguishers using carbon tetrachloride be dangerous? How about other chemical extinguishers?

13. During the First World War the eminent German chemist Sackur was badly burned and killed by an explosion while investigating cacodyl compounds as poison gases. Explain, with an equation, how such an accident might occur, and indicate a precaution which must be taken in working with such compounds.

14. Tabulate a series of mixtures which would function as explosives of the gunpowder type.

15. Of what value are smokes and smoke screens for military purposes in connection with the Army and Navy and their air services?

CHAPTER 4

Nitrocellulose and Other Nitropolysaccharides

Source of Nitrocellulose. Nitrocellulose is made by the ordinary process of nitration using mixed acid and cellulose. Cellulose is the principal component of the tough or woody part of all plants. Any variety of cellulose may be used as raw material, and many varieties are used, for the numerous products commercially made from nitrocellulose. The industries based on cellulose are among the largest of the chemical family and include foods, textiles, paper, construction, explosives, films, artificial silk, artificial leather, lacquers, plastics, and textile processing. For explosives, linters (a short-fiber cotton) is preferred as raw material, although other celluloses may be and are used. Nitrocellulose in general is also called pyrocellulose and guncotton, which names refer to the higher nitrates, and pyroxylin.

Historical Note. Nitrocellulose was first prepared by Pelouze in 1838. Schoenbein, about 1845, advocated it as an explosive on a practical scale and it received much attention. Early production in Austria resulted in serious accidental explosions and it was nearly abandoned. Sir Frederick Abel undertook to manufacture and study it at Waltham Abbey in England, where explosives had been made since early days. He found that the danger was largely due to improper purification from the acid, and as the result of introducing proper purification methods Abel developed a large industry.

About this time Schulze introduced nitrocellulose for small-arms powders, and the E. C. powders were produced. In 1886, Vieille in France, colloided nitrocellulose with alcohol and ether, and rolled the resulting gummy mass into sheets, which were then cut into squares and dried, thus producing a compact, slow-burning, satisfactory propellant. Contemporaneously, Alfred Nobel developed ballistite, a low-nitrated cellulose colloided with nitroglycerine. The final step was cordite, a highly nitrated cellulose colloided with acetone, although it also contained nitroglycerine and vaseline.

The outstanding smokeless propellent explosives today are single-base powders (nitrocellulose colloided with alcohol and ether, or with acetone) and double-base powders (gelatinized nitrocellulose with nitroglycerine). Double-base powders have a somewhat higher explosive potential than single-base powders. The former have the disadvantage that they corrode and foul the gun barrel relatively more, and they are chiefly used in the United States today for small arms.

Cellulose. Certain aspects of the chemistry of cellulose are of great importance in the manufacture of nitrocellulose. Chemically, cellulose is a carbohydrate which forms the cell walls of plants. In the more woody parts it is linked up with materials known as lignins to form lignocelluloses, and that of other parts is sometimes called cutocellulose and adipocellulose. Cellulose can be made from wood by boiling with about 10% NaOH or $Ca(HSO_3)_2$ solution, which is the basic step in papermaking. In this process,

$$\text{Lignocellulose} + \left\{\begin{array}{l}\text{NaOH or}\\ \text{Ca(HSO}_3\text{)}_2\\ \text{solution}\end{array}\right\} \rightleftharpoons \text{Cellulose} + \left\{\begin{array}{l}\text{Solution containing}\\ \text{decomposition products}\\ \text{of lignin.}\end{array}\right\}$$

The cellulose remains undissolved and may be separated by passing the liquid mixture over screens through which the liquor passes, leaving crude cellulose in the form of sheets, which when dried are a commercial product known as lap, or paper pulp. Certain plants, cotton for one, have parts which are sufficiently pure cellulose to use directly, with some purification. Raw cotton is about 91% cellulose. High-grade filter paper is practically pure cellulose.

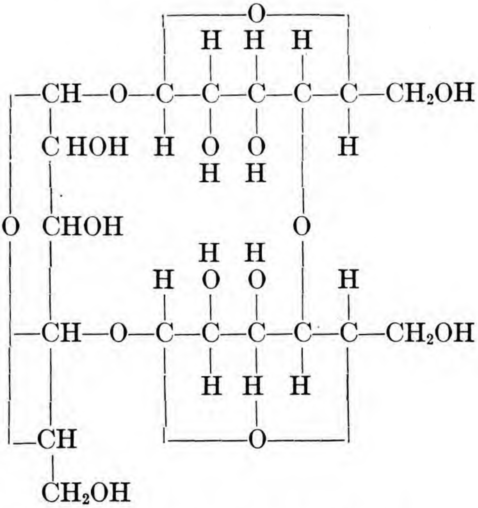
Pure cellulose contains C 44.4%, H 6.2%, and O 49.4%; these proportions yield the empiric formula, $C_6H_{10}O_5$, but the molecular weight of cellulose, although thus far not exactly determined, is certainly much higher than that formula necessitates, probably about 3,000 times; accordingly the formula $(C_6H_{10}O_5)_x$ is employed. Cellulose is a class name rather than a single compound, but all celluloses give similar reactions of a carbohydrate nature, and are regarded as polysaccharides. On acid hydrolysis cellulose yields glucose, perhaps entirely, and a hypothetic mode of formation naturally suggests itself:

$$x\, C_6H_{12}O_6 \rightleftharpoons (C_6H_{10}O_5)_x + x\, H_2O$$

It therefore presents, in an even more complicated form, the usual problems of carbohydrate chemistry,[1] which are also of importance in the question of the constitution of nitrocellulose:

(a) The nature of the lactone linkage.
(b) The nature of the interunit linkage.
(c) The matter of stereoisomerism.

The older synthetic methods of investigating some of these problems have been supplemented in this field by X-ray studies, which seem to indicate that the cellulose aggregates consist of crystallites; and some of the evidence is in favor of a fundamental unit consisting of three glucose residues in a ring. It is possible that the cellulose unit is:



Among the properties of cellulose which are of importance from our standpoint are:

(a) It contains a number of hydroxyl groups which are alcoholic and can be esterified.

(b) It is soluble in ammoniacal copper salt and zinc salt solutions, and in a mixture of NaOH and CS_2. These solutions are starting materials in methods for making artificial silk, and solubility may be due to the OH group. The aqueous solutions are probably of an aquocomplex type, and the third is possibly the xanthate reaction:

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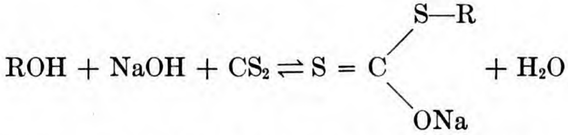
[1] The synthesis of a cellulose was claimed for the first time in 1942.



$$ROH + NaOH + CS_2 \rightleftharpoons S = C\begin{matrix} \diagup S-R \\ \diagdown ONa \end{matrix} + H_2O$$

(c) Cellulose is quite stable to dilute alkali, but with stronger solutions, for example 10% to 20% NaOH, it swells and its fibers acquire a luster like silk. This is the mercerizing process. Some of the alkali is firmly retained, whether absorbed or chemically combined.

(d) Acids when concentrated parchmentize cellulose; less strong acids hydrolyze it to glucose; the concentrated acids may also esterify. Dilute acids hydrate cellulose, and although the nature of the product is still unknown, hydrated cellulose differs markedly from the original; it may reduce Fehling's solution, nitrate much more readily than it does without hydration, and be soluble in sodium hydroxide. Cellulose is very readily hydrated, not only by acids, but also by strong solutions of certain salts, as $Ca(CNS)_2$, and merely by mechanical beating with water. It may take on as much as nine times its weight of water to form a gelatinous mass, which, however, does not disperse in water. The phenomenon is regarded as colloidal and physical rather than as chemical combination, but relatively small degrees of hydration produce anomalous effects in the manufacture of nitrocellulose.

(e) Cellulose is oxidized readily by many oxidizing agents, as the various bleaches, producing oxycelluloses. Oxycelluloses contain free aldehyde groups, reduce Fehling's solution, hydrolyze readily, and are similar to hydrocellulose in behavior. Oxidation reduces the strength of the fiber and the disintegration of fabrics and paper is sometimes ascribable to excessive or improperly controlled bleaching.

The Chemistry of Nitrocellulose. The nitration of cellulose is essentially the esterification of one or more hydroxy groups with nitric acid, and the product is not a nitro compound, except by common usage, but a nitrate ester. The general reaction might be written:

$$(C_6H_{10}O_5)_x + y\ HNO_3 \rightleftharpoons y\ H_2O + [C_{6x}H_{10x-y}O_{5x-y}(NO_3)_y]$$

This equation avoids the difficult questions of the actual structure of cellulose and has some utility in solving practical problems relating to yield and spent-acid concentrations. The older viewpoint was that the course of the reaction was represented by:

$$[C_6H_{10-z}O_{5-z}(OH)_z]_x + y\ HNO_3 \rightleftharpoons y\ H_2O + [C_6H_{10-z}O_{5-z}(OH)_{z-y}(NO_3)_y]_x$$

This equation involves the notion that z is the same for each structural unit, and a further conclusion was that the alcohol-ether–soluble nitrocellulose was a dinitrate, $[C_6H_7O_2(OH)(NO_3)_2]_x$, and the acetone-soluble one was a trinitrate, $[C_6H_7O_2(NO_3)_3]_x$. The present practical approach is, in the first equation, to assign a value to x, usually 4, and then to fix the number of nitrate groups by a nitrogen analysis without regard to position. This procedure is equivalent to assuming for cellulose the formula $C_{24}H_{40}O_{20}$, and then analyses fit the required percentages as shown in Table 13, about as well as would be expected.

It seems probable that the nitration of cellulose never yields a single product, and the problem of producing one of even fairly constant properties is largely a question of standardizing the variables. This must be very carefully done if the desired result is to be obtained. The important variables are the source of the cellulose, the pretreatment of the cellulose (which must have some), the concentration of the mixed acid, the relative weight of cellulose to acid, the temperature, the time of contact of cellulose and acid, and the method of purification of the product. The commercial process later described yields a product employed in the production of smokeless powder and contains 12.6% N ± 0.1%. The maximum thus far introduced experimentally is about 14.4% and the different products are commonly indicated by their nitrogen content.

Experiment. *Laboratory Preparation of Nitrocotton* (12.6% N) (*Pot process*). Weigh out 10 grams of good-quality hospital cotton to 0.1 gram. Boil for ½ hour in a 2% NaOH solution. Wash thoroughly with hot water, dry on a steam bath, and finally in the drying oven at 105°C. (The usual commercial bleaching is here omitted.)

Prepare 400 cc. of mixed acid calculated to contain H_2SO_4 63%, HNO_3 21%, water 16%. (Using HNO_3 of specific gravity 1.5 and 20% fuming sulphuric acid, 100 grams of mixed acid would be gotten from about 32 cc. of H_2SO_4, 15 cc. HNO_3 and 18 cc. H_2O.)

Place the acid, which should be at a temperature of 25° to 30°C., in a 500-cc. beaker and stir in the cotton with a glass stirring rod. Allow it to digest for 30 minutes. Remove the cotton with the stirring rod and wash it several times in fresh portions of cold water. Boil it for four 15-minute periods with four portions of fresh water. (The commercial time is here greatly shortened.) Dissolve 1 gram of Na_2CO_3 in 100 cc. of water. Take 8 cc. of the solution, add to 500 cc. of water, and boil the cotton in it for 15 minutes, and then twice in successive changes of fresh water.

Allow to dry in the air and weigh.

Dissolve 1 gram of the dried preparation in a mixture of 1 part alcohol and 2 parts ether in a beaker under the hood. Pour out a thin layer on a glass plate and allow to dry. Strip off the adhering film. What is it? Allow the remainder to evaporate, then ignite it under the hood to destroy it.

Take a piece of the preparation on crucible tongs and ignite it in a gas flame. Note the results. (Deflagration.)

The remainder may be used later for the KI test, heat test, and a nitrometer nitrogen determination. If so it should be kept in a bottle in which it is covered with water, and dried before use. If not used, it should be burned by igniting under the hood on an asbestos plate with a flame.

In the commercial production of nitrocellulose, because of the fluffy nature of the cotton the ratio of acid to cotton must be relatively high. Higher temperatures have to be avoided because of secondary reactions on the cellulose which may not merely reduce the yield but completely disintegrate the product; and for the same reason the nitrating mixture must not be allowed to stand in contact beyond the time of completion of the reaction. In practice the nitration of the cotton is relatively free from explosive danger, although the product is not thus free and is particularly susceptible to ignition by sparks.

Properties of Nitrocellulose. Nitrocellulose is not a familiar material, for after manufacture it is usually converted directly into its final form as celluloid, photographic film, artificial silk, collodion, smokeless powder, or guncotton. After preparation, careful washing, and drying, nitrocellulose closely resembles the cotton fiber from which it was made, although it is said that in polarized light it exhibits an orange or blue color while cotton shows all the prismatic colors. Since nitrocellulose is a mixture, its properties naturally vary, but the variation is fairly regular with increasing nitrogen content. If ignited by a flame, it flares and burns rapidly (deflagrates). The higher nitrates will explode if burned in quantity. If confined in a closed container, nitrocellulose may explode on ignition, and will explode with full power if detonated. In small quantities, when freshly prepared it may be handled safely, provided reasonable care is exercised to protect it from shock, abrasion between hard surfaces, and sparks or fire.

The specific gravity of nitrocellulose is greater than that of raw cotton (1.58) and increases slowly with increasing nitration to 1.66. The solubility of nitrocellulose in different solvents is a characteristic difference of the different grades, and solvents and approximate solubility are indicated in Table 13. Because nitrocellulose is a mixture, the distinction is never sharp, but between N 8% and N 9.5% nitrocellulose is almost 100% soluble in ether-alcohol. The viscosity of solutions of nitrocellulose in acetone is a function of the nitrogen content and shows a most rapid increase above 13% N. The

TABLE 13

NITROCELLULOSE

Formula $C_{24}H_{40-y}O_{20-y}(NO_3)_y$

%N		%N	Name	Solubility	Use
	← Max—	14.40			
14	← y = 12	14.14	Dodeka—nitrocellulose (old *trinitrocellulose*)		
			Guncotton		
	← = 11	13.47	Endeka—	Acetone	
			Pyrocellulose		Guncotton
13					Smokeless powder
	← = 10	12.75	Deka—		
					Collodion cotton
12					Artificial leather
	← = 9	11.96	Ennea—		Lacquers
					Silk
					Photo film
11	← = 8	11.11	Okta— (old *di*—)		
					Plastics
	← = 7	10.18	Hepta—		
10				Alcohol + ether	
	← = 6	9.15	Hexa—		
9					
			Pyroxylin		
8	← = 5	8.02	Penta—		
7				Alcohol	
	← =	6.76	Tetra— (old *mono*—)		
6					

hygroscopicity of nitrocellulose decreases with increasing N content, and at ordinary temperatures is about 2% for $N = 12.6\%$.

Nitrocellulose is an essentially unstable material which decomposes on aging with the evolution of oxides of nitrogen. Frederick Augustus Abel designed the test named after him, for testing the chemical stability of explosives, based on the detection of the oxides of nitrogen by the use of starch-potassium iodide, or better starch-zinc iodide. An electric method of measuring the conductance of a water drop in which the oxides are dissolved has been advanced. The rate of decomposition is markedly increased, as Abel found, by failure to remove traces of acid, which can be done by prolonged boiling with water. It can be definitely traced to certain impurities, such as resins, and has been ascribed to the lower nitrates. Some impurities which do not impair stability will nevertheless yield a pyrocotton which will give poor tests (for example, nitroalkyls). The decomposition cannot be completely stopped, but for any given variety of nitrocellulose can be reduced to a minimum, and the material is then said to be stabilized. To reach this condition may require as much as 100 hours of boiling with water. It is more difficult practically to stabilize the higher nitrates.

The accumulation of oxides of nitrogen further accelerates the decomposition. The nitrocotton may be further stabilized by the addition of materials to react with the oxides of nitrogen, and diphenylamine is used for this purpose, to the extent of about 1% by weight. In the presence of NO_2, this compound undergoes a series of changes, and is effective for its purpose to the end:

$$\phi_2NH \rightleftharpoons \phi_2N{=}NO \rightleftharpoons C_6H_4(NO_2)N(NO)\phi \rightleftharpoons (C_6H_4NO_2)_2NH \rightleftharpoons C_6H_4(NO_2)NHC_6H_3(NO_2)_2$$

One molecule of diphenylamine will thus dispose of three gram atoms of nitrogen, which is a relatively considerable quantity. Formerly, dyes such as rosaniline were added and instability was judged by the change of color—in this case from red to yellow—due to the acidic reaction as decomposition progressed. This method was a use of merely indicator action, while in the case of diphenylamine the presence of the other products does not indicate impaired stability. Until it is completely nitrated, the nitrocellulose is stabilized. Deterioration of smokeless powder in storage is therefore tested by having a strip of

N/10 methyl violet paper in the storage box. If the strip is bleached in 12 months or less the material is considered too dangerous for continued storage and is disposed of. Various other materials have been suggested as stabilizers, for example, tartaric acid, phenanthrene, nitronaphthalenes, phthalide, certain urethanes (centralite), and the like. In general, the amount required is larger.

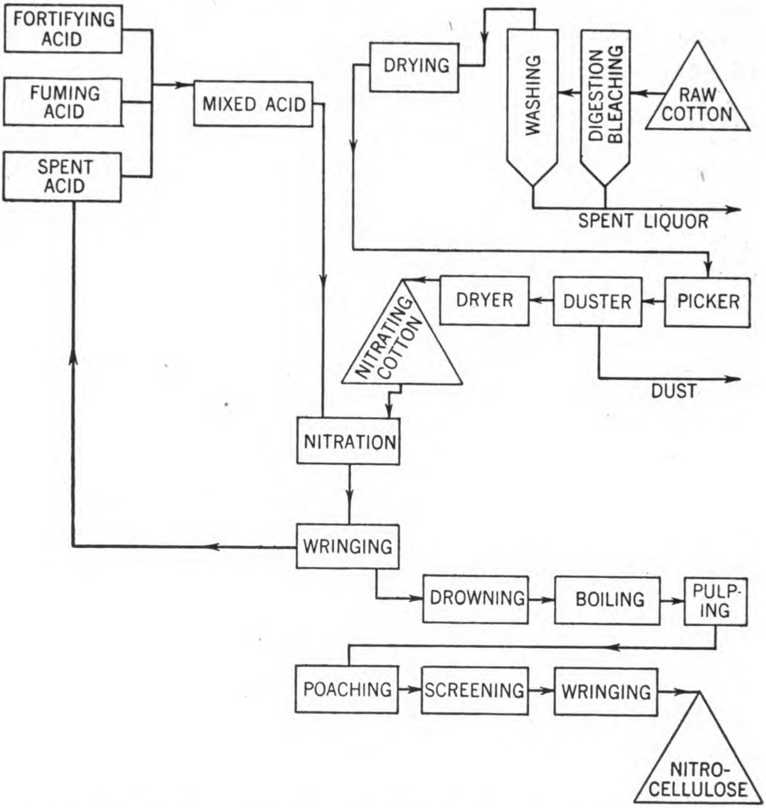


FIGURE 7: **Flow Sheet for the Manufacture of Nitrocellulose**

Commercial Production of Smokeless Powder Nitrocotton.[2] The important steps are: purification and preparation of the cotton; nitration of the cotton; and stabilization, that is, purification of pyrocotton from traces of acid and lower nitrates (see Figure 7).

Linters is preferred, or other cotton or wood pulp supplies the raw cellulose, which is cooked in a digester for about 6 hours with a solution of about 10% caustic soda at a pressure of about 72 pounds per square inch, which corresponds to a temperature of 152°C. The digester is essentially a vertical, cylindrical steel boiler with conical ends, similar to that used in making wood pulp. The caustic liquor is then removed by washing, and the cotton is completely bleached as rapidly as possible, at 36°C. with a 2½% solution of commercial bleaching powder. Excess bleach is then destroyed by the addition of sulphuric acid in minimum quantity and the charge is washed free of the reagents and dried. This treatment removes vegetable oil, resinous materials, and other extractible substances whose presence in nitrocellulose would decrease its stability. Excessive treatment will increase the content of hydrocellulose and oxycellulose and impair the evenness of nitration. These are, as has been noted, soluble in sodium hydroxide, and United States Army Specification 50–11–44 calls for a test of alkali-soluble material in cellulose.

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[2] Adapted from U. S. A., TM 9–2900 (1940), *Military Explosives.*

For even nitration, cotton must be of uniform low moisture content and physical condition, free from lumps and foreign material; hence it is *picked* by machine to reduce it to a fluffy state. It is then blown by an air blast into a large flue leading into the *drying* room, where it is further fluffed out and the fibers are separated from the heavy dust. The dust is removed.

There are two systems of drying in use. In the *continuous drier* the cotton is conveyed by a belt through a long chamber heated to about 100°C. Cotton issuing from the drier is weighed directly into metal containers and transferred to the nitrating house. Entering cotton contains about 8% moisture which is reduced by treatment to about 0.5%. The *chamber drier system* takes longer and is more expensive in operation. Each drying chamber holds about 2,500 pounds of cotton. The chamber is filled and closed tightly; then the temperature is gradually raised to 105°C., where it is held for 24 hours. After a laboratory test of the cotton shows less than 1% moisture, it is weighed in lots of 32 pounds in closed fiber containers and transferred mechanically to the nitrating house.

Three kinds of acid are used in the nitration process: (1) fuming sulphuric acid of 104% (= 20% SO_3) strength; (2) spent acid, which is the acid recovered after nitration; and (3) fortifying acid, which is used to regenerate the spent acid with the addition of some of (1).

Fortifying acid contains 50% to 55% HNO_3, and 45% to 50% H_2SO_4 and supplies all of the HNO_3 required for a new nitration, and a part of the H_2SO_4, the fuming H_2SO_4 supplying the remainder. The mixed acid originally is made by usual procedures, but stirred by iron paddles rather than compressed air.

Four different systems of nitration have been used in the United States: the Du Pont mechanical-dipper process, the centrifugal process, the Thompson displacement system, and the Pot process. In this country the mechanical-dipper process has practically displaced the others. The relative concentration of nitrating acid varies with the process, and also with changes in weather conditions, especially temperatures. The sulphuric acid content is maintained nearly constant and the variation in nitric acid is less than 1% and is largely accounted for by the fact that a certain amount of denitration of nitrocotton takes place during warm weather. Unless the nitric acid is increased to take care of this, the resulting nitrocellulose will be below specification for nitrogen content.

A nitrating unit in the *Du Pont mechanical-dipper process* consists of a battery of four iron or stainless steel nitrators. In each cylindrical nitrator are two vertical revolving paddles operating in opposite directions from each other, the motion being from without inward. These paddles consist of a series of horizontal arms so placed upon the post that when set in motion the cotton is quickly drawn beneath the surface of the acid. The charge of each nitrator is about 1,500 pounds of acid at a temperature of 30°C., having a composition: HNO_3, 21%; H_2SO_4, 63%; H_2O, 15.5%; N_2O_4, 0.5%.

After the acid is run in, the paddles are set in motion and 32 pounds of cotton are added. The speed of the paddles is about 60 r.p.m.; nitration continues for about 20 minutes; and then the bottom discharge valve is opened, and the nitrocotton and acid are dropped rapidly into a centrifugal wringer located below the nitrator unit. The wringer rotates at about 300 r.p.m. until the whole charge is in, when the speed is increased to about 1,100 r.p.m. for 3½ minutes. The spent acid is run by gravity from the outer jacket of the wringer into catch tanks where small amounts of nitrocellulose settle out. The spent acid runs from these catch tanks into a blow case, and is either blown into mixing tanks or set aside for denitration or other means of disposal.

The nitrated cotton is forked through a bottom discharge of the centrifuge into an immersion basin below. As fast as the nitrated cotton falls into the basin it is submerged by a heavy stream of water distributed by a fishtail or other device which combines the greatest dispersion of water with the maximum force for submersion. After this washing the pyrocotton, as it is now called, is transferred by means of pumps or by gravity to the boiling-tub house.

The entire chain of operations here requires not more than 35 minutes. Under ordinary working conditions the fumes are negligible, whereas in the other nitrating systems they are always in evidence. From the standpoint of health of operatives, this sytem is much to be preferred, provided proper care is exercised in manipulation of the machinery. The use of precautions is always important because the preparation of many explosives involves health hazards.

In *the centrifugal process,* nitration and separation of the spent acid are both carried out in one device, a nitrating centrifuge. This is filled with the acid (about 1,500 pounds at a temperature of 32°C.); then the weighed charge of 30 pounds of cotton (ratio of acid to cotton, 50:1) is immersed rapidly by means of an iron fork. It is allowed to stand for about 20 minutes with occasional turning over by means of the fork. The drain cock is then opened and the spent acid is separated by centrifuging, after which the charge is forked out and drowned as in the mechanical-dipper process.

In *the pot process,* iron or earthenware pots are used for nitration. The acid, in a ratio to the cotton of 35:1, is sufficient to cover the charge, and the process uses less acid than the two above described. Iron pots take about 4 pounds of cotton; earthenware pots are smaller, holding a charge of only 2 pounds, but they may be emptied by hand, and several pot charges constitute a wringer charge.

The pots are filled with mixed acid of the concentration as before at a temperature of 30°C.; the cotton is immersed and allowed to digest for from 20 to 30 minutes, and the entire contents are dumped into a centrifugal wringer. The pots may be moved and dumped by a two-wheel truck conveyor. The nitrocotton is then forked out of the wringer and drowned.

The spent acid in all these processes is transferred from the wringer to storage tanks, where it is fortified as indicated previously. The pot process yields the weakest acid, with an average composition of

HNO_3, 18%; H_2SO_4, 65%; H_2O, 16.5%; N_2O_4, 0.5%. Compare this with the starting strength given above.

Purification of Pyrocotton. This process includes the following sequence of processes: preliminary boiling, pulping, poaching, screening, and wringing. The purpose of the treatment is to secure a product of uniform stability by removing remaining acid, other impurities and, as far as possible, nitrocellulose of low nitrogen content by hydrolysis using boiling acid water which in the preliminary treatment has an acid concentration of 0.1% to 0.3%, calculated as H_2SO_4.

The preliminary *boiling* is carried out in large wooden tubs constructed preferably of cypress and having a false bottom. In the center of each tub is a square wooden duct resting on the false bottom. This duct serves as a heating chamber for the water by carrying a centrally located steam pipe. The water boils in this duct, rises to the top, flows over a false top, and is distributed through perforations onto the charge of pyrocotton. The actual boiling time must be 16 hours. The steam is then turned off, the excess water decanted, the tub refilled, and boiled again for 8 hours. This cycle is repeated until each tub has had a 40-hour boil with not less than four changes of water. Careful attention to details in the boiling-tub house insures to the finished pyrocotton a more satisfactory stability than one in which these details have been disregarded.

The next process, *pulping* or *beating*, has for its object reduction of the pyrocotton fibers to a finer state of division in order to remove the last traces of acidity occluded by the fibers.

The beater or pulping machine most generally used in manufacture of nitrocellulose is the Jordan engine, used similarly in the paper industry. This machine consists of a series of broad-bladed knives set in a conical rotor, by means of which the nitrocellulose fibers, as they are forced through the machine along with a large volume of water, are reduced to the desired degree of fineness. The fineness of the material is indicated roughly when a handful squeezed free of excess water shows a clean break as it is broken in parts. The actual fineness is determined by laboratory test.

Another pulping machine is the Miller duplex beater. Its essential features consist of a fixed set of knives at the bottom of a tube over which revolves a roller which is mounted in adjustable bearings and carries a removable set of knives. The rolls repeatedly draw the pyrocotton between the two sets of knives and thus reduce the material to any desired degree of fineness. A weak sodium carbonate solution is used during this process for the purpose of neutralizing the acid retained within the fibers of the cotton and which is set free mechanically when these fibers are macerated. During the first stage of the treatment, a washer, consisting of a large octagonal box covered with very fine wire screen, is lowered into the pulp to remove a part of the sour water, fresh water being added at the same time. The water thus removed passes to settling basins, where any pulp carried off mechanically is recovered. When the desired degree of fineness has been obtained, the material is ready for the next purifying process.

Poaching. It has been pointed out that in the pulping operation fibers of the pyrocotton are broken down mechanically so that the original physical texture of the cotton is destroyed. Preliminary boiling treatment reduced acidity of the fibers and of the interstitial material, but the pulping process, by macerating these fibers, sets free still more acid. It is therefore necessary to repurify the pyrocotton by boiling. This operation is carried on in the poacher house in a manner somewhat similar to that described in the boiling-tub house, but with the notable difference that the first of the five boiling treatments is carried out in an alkaline solution (1 pound of sodium carbonate—soda ash—to the gallon of water, and 7.5 gallons of this solution for every 3,000 pounds of dry nitrocellulose). All the other treatments are made in a neutral solution. After the boiling treatments the pyrocotton is given at least 10 cold-water washings. During all of these treatments a thorough agitation of the pyrocotton is essential so that it is necessary to employ mechanical stirrers driven by gears and shafting. At this stage of the operation it is necessary for the chemical laboratory to determine: (1) stability of the pyrocotton by KI test and heat test at 134.5°C.; (2) percentage of nitrogen in the pyrocotton; (3) solubility of the pyrocotton in the ether-alcohol mixture; (4) degree of fineness; (5) ash. Details of performing these tests are described in Chapter 11.

Screening. After purifying the pyrocotton as described above, it is necessary to separate mechanically any foreign material or any portions of the product which may not have been properly macerated in the beater house. This separation is accomplished by means of the Packer screen—a large box, the bottom of which is fitted with a brass plate having slits 0.025 inch in width. The pulp is drawn through these slits by suction underneath the screen and any particles too coarse to pass through are returned to the beater house for additional treatment. From the Packer screen the pulp is pumped into one of the large blending tubs where it is stored until needed in the next operation.

The *wringing* operation consists merely in forcing the water out of the pyrocotton by means of centrifugal action. Transference of the pyrocotton from the time of nitration up to this stage of manufacture is accomplished by having it suspended in water. It is the function of the wringers to remove water from the pulp so that the subsequent operation of dehydrating by means of alcohol will be done with a minimum amount of water present.

The wringer consists of a perforated brass basket lined with a 24-mesh copper screen. This basket revolves at a speed of about 950 r.p.m. The time of wringing is about 7 minutes. At the end of this operation another sample is laboratory-tested for remaining moisture, which averages between 26% and 28%.

If the wringers are operated at uniform speed for the same length of time, moisture content will not vary more than 2%. This operation concludes the manufacture of pyrocotton.

Uses of Nitrocellulose. Though the foregoing description covers the preparation of nitrocellulose of nitrogen content 12.6% intended primarily for the production of smokeless powder, the preparation of all forms is essentially similar. The highest nitrations are obtained not with anhydrous acid, but with acid containing 11% to 12% of water. An acid of composition H_2SO_4 63.35%, HNO_3 25.31%, and H_2O 11.34% will produce a nitrocellulose containing 13.92% N, but these highly nitrated celluloses are unstable and on purification by water tend to stabilize at about $N = 13.5\%$ which, it is accepted, corresponds to $C_{24}H_{29}O_9(NO_3)_{11}$. The esterification reaction is essentially reversible, and the nitrate groups can be removed by hydrolysis. Removal is almost complete if NaOH is used, but the cotton fiber at low nitration is physically altered to resemble silk and this is one process for making artificial silk. Higher temperatures likewise do not increase degree of nitration, but tend to reduce the yield and ultimately to disintegrate the cellulose entirely.

The highly nitrated celluloses are high explosives, but their fluffiness and lightness of packing as such does not make them especially suitable directly. They may, however, be compressed by pressure to a volume density as high as 1.4 and are used as the main charge in submarine depth bombs. The lower nitrates have the variety of uses already indicated. A solution of nitrocellulose in alcohol and ether is collodion. This solution, with camphor incorporated and dried, is celluloid. The solution may be worked into fibers and denitrated with alkali to yield one variety of artificial silk; it may be dried directly into tissue; or with a variety of other incorporations it may yield the pyroxylin plastics. These nitrocellulose solutions are typical colloid solutions, and yield characteristic gels. Many substances will colloid nitrocellulose—alcohol-ether mixture, acetone, nitroglycerine, and organic nitroliquids in general such as nitrobenzene, T.N.T., and the like.

When ignited unconfined, even the highly nitrated celluloses burn, and burning is a convenient and safe way to dispose of them; but the danger of explosion increases with quantity, as the poor heat conduction may cause the heat to accumulate. They catch fire very readily from sparks, and are often used in fuzes to catch the flame of an electric heating unit. Nitrocellulose detonates readily with moderate amounts of all the common detonators, and the explosive reaction may follow a number of paths (p. 24). The heat of explosion (Q_v) per kilogram is 1,100 to 1,300 Calories, and the explosion temperature 2,710°C. The ignition temperature varies from 183° to 190°C. The velocity of detonation has been measured from 3,700 to 6,200 meters per second, depending on the density. When dry, nitrocellulose explodes under the 2-kilogram weight at about 25 centimeters; with 15% of water at about 85 centimeters; and with over 20% it is completely safe. The velocity of combustion is of the order of 10 meters per second, but varies widely with pressure. For purposes of calculation this explosion equation may be used:

$$2\ C_{24}H_{29}O_9(NO_3)_{11} \rightarrow 41\ CO + 7\ CO_2 + 29\ H_2O + 11\ N_2$$

When detonated at comparable loading densities, pyrocellulose compares favorably with nitroglycerine.

Starch as a Source of Explosives. Any carbohydrate may be nitrated more or less similarly to cellulose to yield explosive material. Starch is a practically useful one.

Starch is a carbohydrate, a polysaccharide, of the same general nature as cellulose, and we may assign it the formula $(C_6H_{10}O_5)_y$. It is prepared on a large scale from a variety of plants such as potato, wheat, corn, barley, tapioca, sage, arrowroot, and others that contain 20% to 80% starch. When pure it is a white powder which, under the microscope, appears as granules which are characteristic of the source and can be identified. For explosives, cassava or tapioca starch is preferred to corn starch. Ordinary wheat flour is principally a mixture of starch and a protein material, gluten, and starch may be extracted from it in the laboratory with water.

The starch granule is not chemically homogeneous, and consists essentially of two carbohydrates which vary in proportion in different starches; the outer portion is called amylocellulose, and the inner, which appears to be a liquid, is known as granulose or amylopectin. Starch is not soluble in cold water, but on being warmed the cells swell up and ultimately burst, whereupon the starch distributes itself in the water colloidally to form a solution (starch paste) which at only moderate concentrations sets on cooling to form a gel. On hydrolysis with acid, starch yields first a readily soluble product known as dextrin, and continued hydrolysis decomposes it very largely into dextrose, which is a commercial procedure. A familiar and sensitive identification reaction for starch is the blue color it yields with dilute iodine solution, which however appears to be due to one of the products of hydrolysis, since raw starch under these conditions frequently gives a brown or black color. In using the test it is well to warm the starch solution slightly first to effect the hydrolysis. The chemical nature of the blue substance is uncertain.

Nitration of Starch. Starch can be nitrated very similarly to cellulose with similar results. In the commercial process the essential steps are:

Purification. The starch is treated to remove fats, oils, and water soluble material and then dried carefully at low temperatures.

Nitration. Purified starch is fed slowly into the acid mixture in a nitrator with agitation and cooling. The temperature is maintained at about 30°C.; the acid concentration is the same as for nitrocellulose, but the acid-to-starch ratio is considerably lower.

Separation and purification. The nitrated starch is separated from the spent acid, drowned in water, washed thoroughly to remove all traces of free acid, and then separated from the water in filters or centrifugal wringers.

Drying. From the wringer the nitrostarch is spread in trays to dry in dry houses heated with air at a temperature of 35° to 40°C. This is the only very dangerous operation, as the dry product is highly inflammable and will ignite from the slightest spark, as of a static charge, to burn with explosive violence.

Mixing. Nitrostarch is incorporated with other things in practical explosives, known in general as "dope." All of the dope materials are ground to the proper degree of fineness and dried to the proper moisture content so that the final explosive will not have too much moisture. The mixing operation is conducted in large revolving mixing barrels. Granular nitrostarch explosives, such as grenite, are sprayed with a solution of the binding material in the mixer, and the resulting granules are dried and screened to the proper size.

Properties of Nitrostarch. Nitrostarch, like nitrocellulose, may contain varying proportions of nitrogen, but for military explosives the prescription is at least 12.8%. Nitrostarch is a white finely divided material, which even under the microscope is similar to starch. It does not, however, give a blue color with iodine, is insoluble in water, and does not form a paste or gelatinize on heating. It is soluble in acetone, and increasingly with the nitrogen content soluble in alcohol-ether, but likewise does not gelatinize with these solvents as does nitrocellulose. It is not very hygroscopic but will absorb water up to 2%.

The decomposition equation is similar to that for nitrocellulose. Its ignition temperature is 170° to 175°C. Under a 2-kilogram weight it explodes at about 50 centimeters of fall, which shows it to be more sensitive than T.N.T. but less so than dry nitrocellulose. Nitrostarch ignites very readily from sparks to give very rapid deflagration. It is readily detonated by the usual detonators (a No. 6 blasting cap is ordinarily sufficient), and is a powerful *brisant* explosive, similar to nitrocellulose.

Nitrostarch is difficult to stabilize and originally was not regarded as practically satisfactory because of instability and sensitivity, but by incorporation with other things satisfactory military and practical explosives are made from it. Propellent powders are not yet practically made from it.

TABLE 14

COMPOSITION OF TROJAN EXPLOSIVE AND GRENITE

Substance	Trojan explosive, %	Grenite, %
Nitrostarch	23.0–27.0	95.00–98.50
NH_4NO_3	31.0–35.0	
$NaNO_3$	36.0–40.0	
Charcoal	1.5– 2.5	
Heavy hydrocarbons	.5– 1.5	
Antiacid ($NaHCO_3$)	.5– 1.5	
Diphenylamine	.2– .4	
Moisture	0– 1.2	0– 1.00
Petroleum oil		.75– 2.00
Gum arabic		.75– 2.00

Grenite and Trojan explosives are two explosives made from nitrostarch which for military use have the limiting compositions, found in Table 14.

Trojan Explosive. This has a grayish black color, is of the consistency of brown sugar, has a damp feel, and a tendency to pack under compression. Treatment with oil reduces its sensitivity to shock, but it is hygroscopic and care must be used in loading to avoid too great absorption of moisture. Trojan is less sensitive and less easily ignited than straight nitrostarch, but burns on ignition. It is used for grenades and trench mortar shells, and is loaded by "jarring" the granular material into the container.

Trojan explosive is somewhat similar to T.N.T. in action, especially in the formula evolved for commercial work, which has $Ba(NO_3)_2$ instead of NH_4NO_3 and a somewhat higher nitrostarch content. It can be consolidated in blocks.

Grenite. This is used only for grenades. It is granular and free running. It is considered too sensitive for other military uses.

Nitrostarch Explosives in General. All nitrostarch explosives present a very definite fire risk; explosion can occur by impact, as they are sensitive, and the burning may be explosive. They should be stored at low temperatures to reduce decomposition, and a dry atmosphere is necessary to avoid absorption of water. Trojan explosive on long standing will corrode metal parts, and is too hygroscopic for bulk storage in wooden containers. Poisoning is not a hazard with these explosives.

Analysis of Nitrostarch Explosives. The following scheme of analysis is prescribed for Trojan explosive by United States Army requirements. It may be appropriately modified for the nitrostarch explosives.

Moisture. Approximately 5 grams of the sample, accurately weighed out, are spread evenly on a 90-millimeter watch glass ($3\frac{1}{2}$-inch diameter) and placed in a desiccator over concentrated sulphuric acid. Loss in weight after 48 hours is taken as moisture. As an alternative method, a vacuum desiccator may be used with sulphuric acid (specific gravity 1.84) as a desiccating agent in a vacuum of at least 700 millimeters of mercury. After 24 hours the vacuum is slowly relieved and the loss in weight taken as moisture.

Ether extract. Approximately 10 grams of the sample are accurately weighed out and placed in a porous crucible (Gooch crucible with thin asbestos mat, or an alundum filtering crucible) and extracted with pure petroleum ether of 0.640 to 0.660 specific gravity. After complete extraction the crucible and contents are dried by means of a stream of dry air until complete removal of the petroleum ether, after which the crucible is placed in a steam oven and dried to constant weight at approximately 70°C. The difference in weight between the original weight of the sample and after extraction is taken as the weight of heavy hydrocarbon oil present, together with the diphenylamine. The diphenylamine in this mixture may be determined by means of the Dumas method for determining nitrogen.

Water extract. The material in the crucible after removal of the heavy oil consists of nitrostarch, ammonium nitrate, sodium nitrate, charcoal, and sodium bicarbonate. By treatment with warm distilled water the ammonium nitrate, sodium nitrate, and sodium bicarbonate are removed, and the material in the crucible, after being dried at 80°C. for several hours, consists of nitrostarch and charcoal. The loss in weight in the water extraction is determined and also the weight of the crucible plus nitrostarch and charcoal. These two measurements are then used in the subsequent calculations.

Sodium bicarbonate. The water extract is made up to a fixed volume. One portion is taken for the determination of the sodium bicarbonate present. This is determined by titration with *N*/10 sulphuric acid, using methyl orange as an indicator, and the alkalinity so found is calculated to sodium bicarbonate.

Ammonium nitrate. At the option of the inspector, the percentage of ammonium nitrate is determined by taking an aliquot portion of the water extract, adding caustic soda until the solution is strongly alkaline, and then distilling in an apparatus as used for ammonia determinations and collecting the distillate in a known volume of standard sulphuric acid. The excess acid is titrated with standard alkali, methyl orange being used as an indicator, and the result is then calculated to ammonium nitrate.

Sodium nitrate. An aliquot part of the water extract is acidified with nitric acid and the solution is evaporated to dryness in a platinum dish. It is then ignited at a low red heat over a suitable flame, using care to avoid loss of the contents. The weight is then taken, a correction is made for the amount of sodium bicarbonate present, and the result is regarded as the amount of sodium nitrate present. Following this procedure, the ammonium nitrate should be taken by difference in order to avoid the determination of ammonia.

Charcoal. The residue in the crucible after the water extraction consists of nitrostarch and charcoal. This material is best extracted in a Wiley extractor with warm acetone until no further soluble material is obtained. The crucible is then dried in a stream of dry air and further dried for several hours at 100°C. The weight of the charcoal is taken as the increase in weight of the crucible over its original weight empty.

Nitrostarch. The difference between the sum of the weights of nitrostarch and charcoal, as determined above, and the percentage of charcoal, as found above, represents the amount of nitrostarch present.

Discussion Questions and Exercises

1. Name as many plants as you can which are important sources of cellulose.

2. Find out what are the various commercial grades of cotton, and describe them.

3. Report on the history of nitrocellulose as a commercial explosive.

4. Review the biosynthesis of carbohydrates in nature.

5. Is the formula for the cellulose unit given on p. 60 consistent with the fact that cellulose can be nitrated up to 14.4% nitrogen, if the assumption is made that nitration involves only esterification?

6. Review the properties of colloid gels and describe some of the properties you would expect gelatinized nitrocellulose to possess.

7. Assuming smokeless powder nitrocotton, N = 12.6%, to be composed of the two nearest compounds, calculate its percentage composition in terms of them (Table 13).

8. Name the principal impurities from which powder nitrocotton should be freed.

9. Why are impurities which do not impair the keeping qualities of nitrocotton, but which give it a short Abel test, objectionable?

10. Define carefully stabilization as applied to nitrocotton.

11. Describe the chemical changes which probably occur in cotton during the preparation for nitration.

12. Taking the original mixed-acid concentration for nitration as given in the text, on the basis of the acid-to-cotton ratio, taken as a round number, calculate the concentration of the spent acid in each process on the assumption that the product in each case contains N = 12.6%.

13. What are the essential chemical changes which probably occur in the stabilization of nitrocotton?

14. From memory, make an outline of a process for producing nitrocotton.

15. Describe pyrocotton as an explosive in accordance with the outline on p. 23.

16. Find out what are the differences in appearance of different types of starch grains under the microscope.

17. Develop a flow sheet for the production of nitrostarch.

18. Contrast nitrocellulose and nitrostarch as explosives.

19. Would you say that these are cheap or expensive explosives?

20. What principles generally applicable to explosives do you find illustrated in the formulas for Trojan explosive and grenite?

21. What is meant by "volume density"? (Consider the fraction of the volume occupied by air space.)

CHAPTER 5

Nitroglycerine and Related Explosives

Nitroglycerine [$C_3H_5(NO_3)_3$]. Nitroglycerine is the trinitrate ester of the triatomic alcohol, glycerine. At ordinary temperatures the pure compound is a water-white, oily liquid, while the commercial variety is usually pale yellow to brown. It has a faint odor which becomes more evident with a slight rise in temperature, and is usually described as having a sweet, burning taste. Its vapors are definitely toxic, producing headaches which in mild cases are relieved by fresh air, and this toxicity is an industrial hazard for which provision must be made. Nitroglycerine is readily and strongly absorbed through the skin and is highly toxic if taken internally in any quantity. In small doses, however, it is used in medicine for certain cardiac conditions and in its physiological reaction is similar to alkyl nitrites.

The specific gravity of nitroglycerine is 1.60 at 15°C., varying about $-.001$ per degree Centigrade; viscosity, about 2.5 times that of water; index of refraction, $N_D = 1.4744$; and its vapor tension is 0.00025 millimeters at 20°C. and 0.29 millimeters at 100°C. It begins to decompose at 140°C. and cannot be distilled without decomposition even in a vacuum. It crystallizes in two solid forms which exhibit monotropic allotropy, and are known as the stabile and labile modifications. Because of the phenomenon of supercooling, each exhibits slightly different melting and freezing points, which have been carefully investigated, notably by S. Nauckhoff[1] and H. Kast,[2] and the accepted melting point values are: labile 2.8°C., stabile 13.5°C. The suggestion has been made that these forms are chemical isomers of the formulae:

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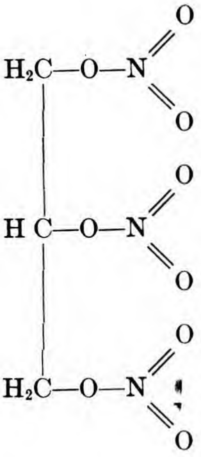
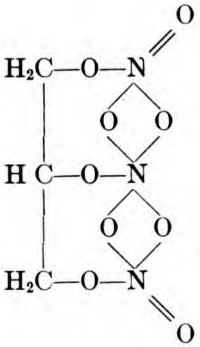
[1] Nauckhoff, *Z. angew. Chem.*, 1905, 11; *Z. Schiess- u. Sprengstoffw.*, 1911, 124.

[2] Kast, *Z. Schiess- u. Sprengstoffw.*, 1906, 225.





The stabile isomer crystallizes in the rhombic system and the labile in the triclinic system.

Nitroglycerine is an excellent solvent, and its solvent properties have been the subject of much investigation, particularly in relation to the modern theory of solution. At ordinary temperatures it is miscible in all proportions with methyl alcohol, acetone, ether, chloroform, benzene, various nitro compounds, and a variety of other solvents, but dissolves only 43 grams to 100 c.c. in ethyl alcohol at 20°C., where the nitroglycerine phase contains 5.4% alcohol, but at 50°C. ethyl alcohol and nitroglycerine are completely miscible. Nitroglycerine is only partially and slightly miscible with CS_2. Water at 15°C. dissolves 1.6 grams of nitroglycerine per liter.

As an ester nitroglycerine is hydrolyzable by acids and by alkalies, but the alkaline hydrolysis yields a variety of products which do not usually include glycerine; for example:

$$C_3H_5(ONO_2)_3 + 5\ KOH \rightleftharpoons KNO_3 + 2\ KNO_2 + CH_3COOK + HCOOK + 3\ H_2O.$$

Raw Materials for Manufacture. Glycerine is ordinarily obtained by the saponification of fats, but may also be made by various biosynthetic methods, for example from sugar by the Protol process; and from petroleum. The United States Army abandoned nitroglycerine powders as standard in 1906, among other reasons because it was anticipated that under war conditions a shortage of glycerine might develop, and European experience from 1914 to 1918 confirmed this. According to Naoum,[3] dynamite glycerine should conform to the following tests:

Specific gravity should be at least 1.262. Determine by pyknometer at 15°C. Avoid the formation of air bubbles by stirring, as they escape only on long standing.

Neutrality. Shake 50 milliliters of sample with 100 milliliters of distilled water. Add phenolphthalein and titrate with normal acid or alkali. Not more than 0.3 milliliters should be required.

Residue on evaporation and ash. Total residue is found by carefully evaporating to constant weight 5 to 10 grams of glycerine in a platinum dish on a sand or air bath at 160° to 180°C., with the addition of several successive small amounts of water to avoid the formation of difficulty volatile polyglycerines, which can be easily formed if too large samples are used. Total residue should be less than 0.20%. After determining total residue, heat carefully to redness to determine the inorganic residue. This should be less than 0.05%.

Water content and polyglycerines. Water lowers the specific gravity of glycerine and polyglycerines raise it. The presence of small amounts of polyglycerines is not harmful unless they mask the presence of water. Water may be determined by allowing a small quantity of glycerine to stand in vacuo in a thin layer over sulphuric acid to constant weight, or by heating 10 grams of glycerine in a loosely covered weighing bottle at 90°C. The bottle should have a circular piece of filter paper between it and the cover. After 1 hour determine the loss in weight, and repeat hourly until it becomes constant and small. Both methods are only approximate.

Mineral impurities may result from the process of manufacture. These should be no more than traces of *chlorides*, *sulphates*, *calcium*, and *arsenic*, by the usual tests of qualitative analysis.

Sugar and glucose should be absent. Their presence may prove deliberate adulteration. Fehling's solution is employed.

Absence of reducing substances. (a) Mix equal volumes of 10% $AgNO_3$ and glycerine and allow to stand 10 minutes. There should be no dark cloud. (b) Mix equal volumes of glycerine and (note the preceding paragraph) Fehling's solution, and fill a flask rapidly and completely with this, so that there is no air between the stopper and liquid. There should be no reduction after 12 hours.

Absence of albumins. Test with lead acetate solution. There should be no precipitate and at the most an opalescence.

Absence of fatty acids. Volatile fatty acids are detected by heating glycerine with alcohol and concentrated H_2SO_4. An ester odor is a positive test. To detect the higher fatty acids, dilute glycerine with twice its weight of water, add nitrous acid, and heat for two hours on a water bath. A precipitate is a positive test. Both should be absent or present only in traces.

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[3] Naoum, *Nitroglycerine and Nitroglycerine Explosives.*

Test nitration. In the plant an important test is the nitration under standardized conditions of about 101 grams of the glycerine and the quantitative determination of the yield of nitroglycerine. In the usual procedure the yield should be 225% or 226% by weight at 30°C. nitrating temperature, and 228% to 229% at 15°C.

The apparatus ordinarily used (Figure 8) consists of a special separatory funnel equipped with outer water cooling, and several inlets to accommodate a glycerine dropping funnel, a thermometer, a tube for air stirring, and an escape tube for the acid fumes. This apparatus may be improvised from the usual laboratory apparatus and used for the preparation of small samples of nitroglycerine.

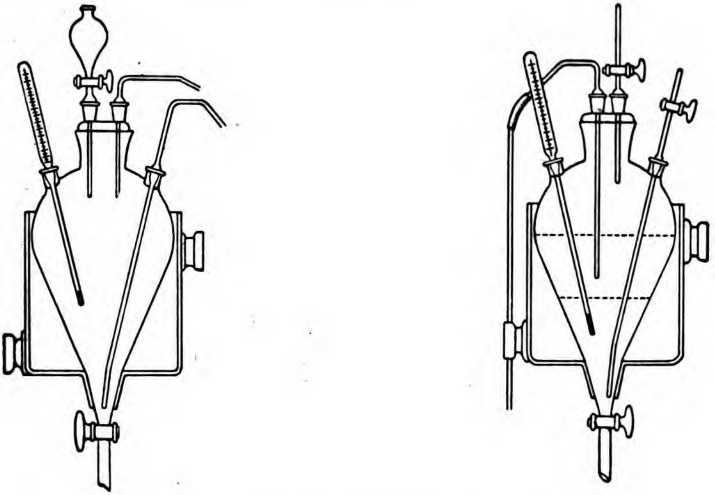

FIGURE 8: **Test Nitration Apparatus for Nitroglycerine**
(Courtesy of Williams and Wilkins Co.)

Place 80 grams of mixed acid (H_2SO_4 60%, HNO_3 35%, H_2O 5%) in the main separatory funnel. Start the air stirrer bubbling steadily. Drop in slowly 10 grams of glycerine, keeping the temperature below 30°C. Allow to stand 20 minutes after addition of glycerine and then stop stirring. After settling, run off the acid, which is the lower layer. Wash three or four times with cold water, returning the lower layer which is now the nitroglycerine to the funnel, once with 5% Na_2CO_3 solution, and twice more with cold water. The nitroglycerine thus prepared will be cloudy, but will clear on standing, and may be dried over $CaCl_2$.

Nitroglycerine should be handled carefully, kept away from metal contact or blows, and should be destroyed by mixing with sawdust and burning (not on metal) as soon as one is through with it. Do not keep it about the laboratory and do not pour it into sinks. It can be safely kept dissolved in methyl alcohol, from which it may be extracted with water. Watch out for small residues which should be dissolved in large quantities of water or boiled with NaOH solution. A *drop* of nitroglycerine allowed to fall upon a hot iron plate explodes violently. It can be readily identified by extraction from a specimen with ether. Evaporate a drop of the extract on filter paper, then strike with a hammer on an anvil. Detonation indicates its presence.

In manufacturing practice, glycerine is nitrated with mixed acid containing usually H_2SO_4 60%, HNO_3 35%, H_2O 5%, by weight, an acid which can be made up from ordinary concentrated sulphuric acid and 93% HNO_3. About 7 to 8 parts of this are used for one part of glycerine. Using oleum, a stronger acid of about 60:40 with almost no water may be used. The requirements are about those for other nitrations and the nitrating acids will be more extensively discussed in a later chapter. One of the reasons for the choice of this acid strength is that, apart from avoiding oxidation, the solubility of nitroglycerine in the spent acid is almost a minimum, and the yield is thereby increased.

Manufacture of Nitroglycerine. In the manufacture of nitroglycerine nitration is first; then follows separation and purification.

The *nitration* operation is highly hazardous. It is performed in a separate building in which no other operation is conducted, and the building is barricaded. The nitrator is a cylindrical vessel, slightly higher than wide, of heavy sheet lead, with a cover containing windows which enable the interior reactions to be seen. It also has openings for glycerine and acid inlet pipes, vapor exhaust pipe, thermometer, cooling-coil inlet and outlet pipe, and compressed-air inlet. Inside, the nitrator has water-cooling coils and a lead compressed-air pipe which admits the air for stirring near the bottom. The bottom of the nitrator is slightly inclined and has a large stopcock at the lower end so that the nitration products can be run off.

The nitrator may also be equipped with a large specially designed "dump valve," by means of which, in the event of sudden decomposition or rise in temperature, the entire charge may be rapidly dropped into a large "drowning tank" located directly beneath and containing four or five times its volume of water. The nitroglycerine may be recovered from here through a stopcock.

The acid and glycerine flow into the nitrator by gravity or pressure from buildings outside the barricade. The acid is first weighed out and run in. The glycerine pipe distributes the glycerine over the surface of the acid. The acid-to-glycerine ratio is 7:1 or 8:1, and from 100 to 500 kilograms may be nitrated at one run. The temperature is not allowed to exceed 30°C., and the yield is better as the temperature is lower, but practical difficulties related to cooling on a factory scale preclude the use of temperatures below 12°C. The nitration time varies slightly with the charge and temperature, but 20 minutes is representative. Stirring is continued for a few minutes after nitration is considered to be complete, and then slowly as the charge is run into the separator.

Separation. With a spent acid of the usual strength, (specific gravity 1.7) the nitroglycerine will separate to the surface reasonably rapidly. Various additions have been patented to expedite separation, after nitration, for example, paraffine, stearic acid, and Na_2SiF_6.

The separator is a rectangular vessel of sheet lead with a conical bottom. It has an air inlet for stirring and windows for observation of the line of separation. The charge comes in on one side. A side faucet at a suitable height enables most of the nitroglycerine to be run off the surface of the acid at once. The acid is then run out of the bottom of the tank, and the remaining nitroglycerine is collected at the bottom and added to the first part. The separator is also connected to the drowning tank.

There are other types of separators and the operations of nitration and separation may be combined and carried out in a combination nitrator and separator.

The separated nitroglycerine contains acid, the major part of which is easily, the last traces difficultly, removed by washing with water. This *purification* is done in cylindrical lead wash tanks or lead-lined wooden tanks, having a sloping bottom and at the lowest point a stoneware stopcock for drawing off the nitroglycerine. At a higher level may be one or more stopcocks to draw off the main body of wash water. The tank is covered, provided with compressed-air agitation and with windows for observation, a thermometer, and sometimes a funnel skimmer connected by a hose to one of the stopcocks to remove the last parts of wash. Its size is such that the charge of nitroglycerine fills it one-third full, and an equal volume of wash is used.

The nitroglycerine is first given a drowning wash of cold water, and then three or four washes at temperature rising to 40°C., with about four minutes of agitation. At this point it may be washed and agitated for 15 minutes with a 2% or 3% Na_2CO_3 solution, at a temperature as high as 50°C. After this it is given several washes with lukewarm water to remove the soda; the final nitroglycerine must be neutral to moist litmus, which indicates satisfactory washing. A sample at this point is also analyzed. For smokeless powder it must be given the "heat test," at 134.5°C and must withstand the Abel or KI test for 20 minutes at 65.5°C.

The washed nitroglycerine is filtered to remove the slimy impurities and foreign substances. This filtration may be omitted. The filters are rectangular lead boxes which hold circular stretched flannel or felt covered with a layer of common salt for a filter medium. After filtration the nitroglycerine still contains water, which renders it milky although it amounts only to about 0.5%. The nitroglycerine is run to storage, where after standing the small amount of water separates and the nitroglycerine becomes perfectly clear.

Filtration concludes the manufacture of the nitroglycerine itself. There are, however, a number of incidental operations in the usual plant; for example, after-separation of nitroglycerine from the quickly removed spent acid; clarification of the wash waters, and denitration and recovery of the spent acid. By various devices of careful procedure, yield of nitroglycerine approaches 95% of that theoretically possible.

The manufacture of nitroglycerine is essentially hazardous and plant design is an important matter. In general one operation is confined to one building, and pipes connecting units have arrangements for disconnection except during actual use. Buildings are barricaded, and connection between two buildings even by zigzag tunnels is avoided. Light construction is safer and cheaper.

Analysis of Nitroglycerine. The following chemical tests are usually made:

Determination of moisture. Use a 5-gram sample and dry to constant weight in a thin layer over $CaCl_2$ in a desiccator. It may be determined by heating to (fairly) constant weight at 45°C. in a shallow dish in air. Turbid nitroglycerine contains from 0.4% to 0.6%, and clear nitroglycerine from 0.1% to 0.2%.

Acidity and alkalinity. Shake a 5-gram sample with 100 cc. of water in a separatory funnel. Test the water with methyl orange or Congo red, and then titrate with 0.1 *N* acid or alkali.

Nitrogen. While several methods are commonly used, such as the Hess method of boiling with ferrous sulphate in sulphuric acid solution, and the Wolff method of decomposition with ferrous chloride and hydrochloric acid in a current of carbon dioxide, the easiest process is the standard Du Pont nitrometer (see page 232) method which is entirely satisfactory.

Stability tests. All of the standard explosives stability tests are made with nitroglycerine: the Abel test using starch-potassium iodide paper, or starch-zinc iodide paper; the various heat tests using methyl violet paper; and the like. The nitroglycerine must obviously at least withstand the tests prescribed for the explosive into which it enters, as for example smokeless powder. Some explosives, as for example dynamite, cannot be given the stability tests directly, for, because of physical subdivision of the nitroglycerine, it may appear to be less stable than it really is, and must be extracted before testing.

Explosive Characteristics of Nitroglycerine. The explosion equation for nitroglycerine is:

$$4\ C_3H_5(NO_3)_3 \rightleftharpoons 12\ CO_2 + 10\ H_2O + 6\ NO_2 + O_2$$

On ignition by an ordinary small flame it does not explode but burns; in quantity, however, it may always explode, particularly if in contact with metal. It may be readily destroyed in the laboratory by mixing with sawdust and burning on an asbestos plate, and quantities too small to collect may be dissolved in large quantities of water or boiled with NaOH solution. The heat of explosion can be calculated theoretically at constant volume with water gaseous as in the neighborhood of 1,485 Calories per kilogram, or 1,595 with water liquid, which agrees with calorimetric measurements. The explosion temperature is variously estimated, but the maximum is 4,250°C., and all values are high as compared with other explosives.

Nitroglycerine is very sensitive to mechanical shock and explodes on a 4-centimeter drop of a 2-kilogram weight. It is readily detonated by a hammer on an anvil when absorbed in filter paper, and this is a convenient method of identification. Frozen nitroglycerine is somewhat less sensitive than the liquid, but a half-thawed mixture is more sensitive than either. Nitroglycerine is readily detonated by any detonator with velocities of detonation up to 8,500 meters per second, and is a powerful *brisant* explosive. Certain nitroglycerine explosives, such as gelatin dynamite, seem to possess the inherent characteristic of detonating with two different velocities—one low, around 2,000 meters per second, and one high, around 7,000 meters per second—depending on various conditions. The actual power developed varies. For example, the Trautzl block (see Chapter 16) expansion of 10 grams of nitroglycerine with various detonating caps is given in Table 15.

TABLE 15

TRAUTZL BLOCK EXPANSION WITH 10 GRAMS OF NITROGLYCERINE

Cap	Expansion, cc.	% power
No. 1	190	32
No. 3	225	38
No. 6	460	78
No. 8	590	100

For use as an explosive, nitroglycerine has certain practical disadvantages which have been slowly overcome in the development of the art, by mixing it with a variety of other things. Some of these considerations may now be presented.

As a liquid nitroglycerine is practically difficult to handle, for usual applications. This condition may be improved if it is converted to a solid by absorbing or adsorbing it in a variety of things, for example kieselguhr, which does not react chemically. Such combinations are known as "inactive-base" dynamites. Wood meal or other combustible substances yield "active-base" dynamites. Colloiding with nitrocellulose yields blasting gelatin.

Nitroglycerine and explosives containing it freeze at moderately low temperatures. The frozen solid is less sensitive, but to thaw it is a dangerous operation, which however is often necessary in practice as the result of freezing of nitroglycerine explosives after improper protection during winter months. Thawing must be done using hot water in a sort of double boiler. This risk can be overcome by mixing with nitroglycerine other explosive liquids to lower the freezing point on the principle of Raoult's Law; nitroglycol, tetranitrodiglycerine, and other substances can be used for this purpose.

Nitroglycerine is very sensitive to shock. This sensitivity may be partially overcome by the admixture of other materials, and all softer substances lower the sensitivity. Nitroglycerine explosives are all very dangerous materials, however, from this standpoint and are in general not practicable for most military purposes. But they can be handled with reasonable care and are the most important explosives for general commercial use.

Nitroglycerine has a very high explosion temperature and a quite persistent explosion flame, which make it unsuitable for gassy and dusty mine work. This hazard may be overcome by mixing in inert substances to lower the temperature of explosion—salt hydrates, or calcium carbonate, for example.

On the other hand, as Nobel was the first to point out, nitroglycerine has, basically, properties very valuable for an explosive—great power and ease of detonation. The other factors are well within reasonable limits and research has solved many difficulties.

Nitroglycerine Explosives. The nitroglycerine explosives may be classified as:

(1) *Dynamite.* Nitroglycerine in an (a) active base, and (b) inactive base.

(2) *Blasting gelatins.* Nitroglycerine colloided with nitrocellulose.

(3) *Gelatin dynamites.* Blasting gelatin with incorporations, similar to the dynamites.

(4) *Low-freezing or nonfreezing dynamites.*

(5) *Permissible dynamites and gelatins,* such as the monobels and duobels.

(6) *Explosives with a low nitroglycerine content.* The role of the nitroglycerine is mostly to increase sensitivity and to ensure propagation of explosion. Many of these are chiefly ammonium nitrate. Some are known as ammonia dynamites.

Table 16 gives some typical formulas.

Manufacture of Nitroglycerine Explosives. The manufacture naturally starts with nitroglycerine. In the case of guhr dynamite, the mixing is done in wooden troughs or boxes, about as high as a table, sometimes lined with sheet lead. Nitroglycerine is poured into the kieselguhr in weighed quantities and given a preliminary mixing by wooden shovels. The mass, consisting of coarse lumps, is rubbed through a coarse screen of about 1½ meshes per centimeter into a

TABLE 16

COMPOSITION OF TYPICAL NITROGLYCERINE EXPLOSIVES

	Dynamite Inactive base	Dynamite Active base 40% "straight"	Blasting Gelatin	Gelatin Dynamite 65%	Non-freezing Gelatin Dynamite	Non-freezing Dynamite	Early Permissible Dynamite	Permissible Dynamite	Permissible Gelatin Dynamite	Monobel
Nitroglycerine	75	40	92–95	63.25–61.5	39	15–25	42–52	25–30	25.5	10
Kieselguhr	25						11–13			
$NaNO_3$		45		27–28	30	50–55		24.5–30.5		
Woodmeal		12		8–7	5	10		39.5–40.5		10
Carbonate + H_2O		3								
Nitrocellulose $(NO_2)_{11}$			5–8	1.75–3.5						
Collodion cotton					2				1.5	
Dinitrotoluene					24					
Tetranitrodiglycerine						15				
Sulphur						0–3				
Rosin						0–2				
NaCl										10
Magnesium sulphate, Sodium sulphate, or Crystallized soda							47–35			
NH_4NO_3									37	70
$K_2Cr_2O_7$								5		
Nitrotoluene									5.0	
Dextrin									4	
Glycerine									3	
KCl									24	

second box. The moist lumps are thus broken up and mixed with dry particles. The rather uniform-appearing mass is then turned over and put back into the first box through a somewhat finer screen of about 3 meshes per centimeter. This second screening gives it fine subdivision and homogeneity. The finished mixture should be loose and crumbly like fresh earth, neither too wet nor too dry, and with no visible nitroglycerine.

In the case of blasting gelatin, nitroglycerine is colloided with collodion cotton made substantially as previously described and containing 12.1% to 12.2% nitrogen. The gelatinizing is done in copper pans, rectangular in shape, holding an ordinary charge of 100 kilograms. The collodion cotton is stirred into the nitroglycerine by wooden shovels, and the temperature is raised by water heating to 50°C. After mixing, the mixture is allowed to stand for about 25 minutes. It is then thoroughly mixed to secure complete uniformity in a mixing machine, of which there are several types. In making gelatin dynamites, the additional materials known as "dope" are first properly prepared and then added to the gelatin in the mixing machine, in the proper proportions.

Experiment. *Laboratory Preparation of 65–35 Gelatin Dynamite.* 125 grams of cold nitroglycerine is weighed into a porcelain casserole and 5 grams of finely screened collodion cotton is well mixed with the cold liquid nitroglycerine. (Nitrocotton previously prepared will do.) The casserole is placed on a water bath and maintained at a temperature of 60° to 65°C. for about 20 minutes, when gelatinization is complete, and the gelatin has the consistency of a thick syrup. Mix 54 grams of potassium nitrate and 16 grams of wood meal or fine sawdust intimately in a porcelain mortar. This is the "dope." Add this gradually to the gelatin, stirring with a horn spatula. Mix the resulting mass in a wooden bowl with a wooden dowel stick, trying to knead it to complete homogeneity like dough. Do not mix it by hand, as nitroglycerine may cause severe headaches by absorption through the skin. The homogeneous mass may be rolled into a cylindrical roll on a board, cut into suitable lengths, and wrapped in cartridge paper. Small residues of dynamite may be dissolved in acetone, the solution mixed with wood meal, and burned on an asbestos plate.

After the mixing operation, in the case of both dynamite and gelatin, the resulting mixture is cartridged by means of a cartridging machine into its usual commercial form. Because of the difference in physical state, the cartridging of dynamite is a tamping operation, while that of gelatin is extrusion, and there are many types of machines. The cartridges of both are cylinders of paper which have been treated with a paraffin composition. The cartridges, or sticks as they are known, are cylindrical in shape and are made in various sizes, but a standard size is $1\frac{1}{4}$ inches in diameter by 8 inches in length. They are then packed in corrugated paper or wooden boxes, a standard weight being 50 pounds per case. The number of $1\frac{1}{4}$-inch by 8-inch cartridges per 50-pound case, which is a measure of the density, is used in practice as the "cartridge count" which may vary from 100 to 200. However, powdery, free running dynamites are also made and packed in bulk packages.

Properties of the Nitroglycerine Explosives. The nitroglycerine explosives are the most powerful of all explosives and are universally used for peacetime work. While they have some military application, their sensitivity is too high for general exposure to normal military hazards, and for any use they require care in handling and protection in storage.

Their characteristics as explosives are essentially those of nitroglycerine, and both dynamites and gelatins are commonly rated on the basis both of nitroglycerine content as 40%, 60%, or the like, and explosive strength. The explosive strength in performance is in general less than that of nitroglycerine, and not always exactly proportional to the nitroglycerine content where other active components are present. Blasting gelatin is an exception in that its explosive strength is higher than that of nitroglycerine and is the highest of all practical explosives, being exceeded only by a few known substances. The 92–8 blasting gelatin has a lead-block expansion for 10 grams of 580 cc. where plain nitroglycerine has 550, and this is a fair test as both are explosives of the same order of detonation velocity.

In Table 17 there is a basis for a general comparison of the characteristics of the nitroglycerine explosives. The practical uses of these explosives will be discussed later (see Chapter 17).

Other Similar Explosive Substances. Nitroglycerine is the nitrate ester of a polyatomic alcohol. Practically all of the homologous and related nitrate compounds can be made by very similar processes. All of them, as well as the true aliphatic nitro compounds, have explosive properties, some of them exceeding nitroglycerine in power. In general they are more or less similar, and while not yet valuable on a large scale, many have interesting uses. Thus sucrose, $C_{12}H_{22}O_{11}$,

TABLE 17

CHARACTERISTICS OF NITROGLYCERINE EXPLOSIVES

Characteristics	Explosives		
	Pure nitroglycerine	Guhr dynamite 25–75	Blasting gelatin 92–8
Heat of Explosion ($Kg-H_2O$ vapor–Q_v)	1,485	1,090	1,560
Explosion Temperature (°C.)	4,250*	3,420*	4,300*
Sensitivity (centimeters of fall of 2-kilogram weight)	4	7	12
Lead-block expansion (10 grams)	550	370	580

* This figure, taken from Kast, is higher than generally accepted.

can be dissolved in glycerine up to 25% by weight and the resulting solution nitrated like glycerine to give an explosive oil containing nitrosugar, which has about the properties of the pure nitroglycerine, but effects a considerable saving of glycerine. This explosive is known as nitrohydrene. Other sugars such as dextrose may be used, and also polyatomic alcohols. Hexanitromannitol now has some applications. Sugar may also be nitrated alone. Some of these compounds, such as nitrochlorhydrin and others mentioned previously, have been used to render nitroglycerine nonfreezing while at the same time not lowering its explosive force greatly. A few such substances are listed in Table 18.

Pentaerythrite Tetranitrate (P.E.T.N. or Pentrit). Of the various compounds listed above, this one is practically important today and is widely used as an initiating explosive, in Primacord; and in certain mixture explosives with T.N.T. and others.

Preparation of Pentaerythrite.[4] 1,940 grams of formaldehyde, or 4.85 kilograms of a 40% solution, and 600 grams of acetaldehyde (1 kilogram of 60% commercial aldehyde) are dissolved in 90 liters of water containing 1,600 grams of slaked lime in suspension. The solution is in a wooden cask, which can be closed, since no pressure changes are encountered in the reaction. The cask is rolled about several times a day in order to bring the lime into sufficient contact with the solution. After about three weeks the reaction is complete.

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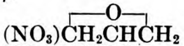
[4] This is an old method described by Naoum.

TABLE 18

EXPLOSIVES SIMILAR TO NITROGLYCERINE

Name	Formula	Mol. Wt.	M.P. °C.	B.P. °C.	Notes
Methyl nitrate	CH_3NO_3	79	liquid	65	sensitive, stronger than nitroglycerine
Ethyl nitrate	$C_2H_5NO_3$	91	liquid	87	less sensitive, weaker than nitroglycerine
n-Propyl nitrate	$C_3H_7NO_3$	105	liquid	110.5	less sensitive than $C_2H_5NO_3$
Isopropyl nitrate	$C_3H_7NO_3$	105	liquid	101	weak
Nitroglycol	$(CH_2)_2(NO_3)_2$	152	-11.5	194	powerful, sensitive, like nitroglycerine
Glycol mononitrate	$C_2H_4(OH)NO_3$	107	liquid	91	powerful
Trimethyleneglycol dinitrate	$(CH_2)_3(NO_3)_2$	134	liquid	211	powerful
Methylglycol dinitrate	$CH_3CH(NO_3)CH_2NO_3$	166	liquid	$92^{10mm.}$	
Erythrite tetranitrate	$(CH_2NO_3)_2(CHNO_3)_2$	310	120		sensitive, powerful
Butyleneglycol dinitrate	$C_4H_8(NO_3)_2$	180	mixture		insensitive
Nitroisobutyl trinitrate	$(NO_3)C(CH_2NO_3)_3$	256	oil		similar to nitroglycerine
Glycerine dinitrate	α or symmetrical	182	26 hydrate		similar to nitroglycerine
Glycerine dinitrate	β or unsym.	182	liquid		
Glycerine mononitrate	α	137	58		explosive but insensitive
Glycerine mononitrate	β	137	54		
Nitroglycide	 $(NO_3)CH_2CHCH_2$ (O bridging)	119	liquid	174	sensitive
Dinitrochlorhydrin α	$ClC_3H_5(NO_3)_2$	200.5		$216^{750mm.}$	sensitive
Dinitrochlorhydrin β	same	200.5		$146^{18mm.}$	
Acetyldinitroglycerine	α	224	liquid		weak, insensitive
Acetyldinitroglycerine	β	224	liquid		
Formyldinitroglycerine	α	210	liquid		more powerful than acetyl
Formyldinitroglycerine	β	210	liquid		
Tetranitrodiglycerine	$[C_3H_5(NO_3)_2]_2O$	346	oil		powerful, sensitive
Hexanitromannitol	$C_6H_8(NO_3)_6$	452	108.5	explodes 120	powerful, sensitive

The solution is siphoned or filtered off and the calcium formate precipitated by oxalic acid, the alkaline reaction changing to acid and the brown color to yellow. (By using a proper hot concentration, the calcium formate, whose solubility is little changed by temperature, can be directly precipitated.)

$$8\ CH_2O + 2\ CH_3CHO + Ca(OH)_2 \rightleftharpoons 2\ C(CH_2OH)_4 + Ca(HCO \cdot O)_2$$

The oxalate is allowed to settle, and the water is driven off under diminished pressure. The crystals obtained on cooling are centrifuged or drained from the syrupy mother liquor. The yield is about 1,200 grams of crude pentaerythrite having a melting point of 235° to 240°C.

For further purification the brown, crude product is stirred with a little alcohol and sucked dry on a filter, leaving the pentaerythrite perfectly white; after several recrystallizations from water an absolutely pure product is obtained. For nitration this is not necessary. Pure pentaerythrite forms tetragonal crystals melting at 253°C., and dissolves in 18 parts of water at 15°C.

Preparation of Pentaerythrite Tetranitrate. Nitration of pentaerythrite cannot be done with mixed acid, and various difficulties, including fire, result from departing from the careful procedure. 100 grams of finely powdered pentaerythrite is gradually dissolved in 400 cc. of nitric acid of specific gravity 1.52, with good cooling to 25° or 30°C. Toward the end of the nitration the difficultly soluble nitrate partly separates. By the gradual addition of 400 cc. of concentrated sulphuric acid of a specific gravity of 1.84 and cooling, it is completely precipitated.

$$C(CH_2OH)_4 + 4\ HNO_3 \rightleftharpoons C(CH_2NO_3)_4 + 4\ H_2O$$

The liquor is allowed to stand for an hour and sucked dry on a filter, the acid being first displaced with a 50% sulphuric acid and then with water. The last traces of acid are removed by washing with dilute soda solution. The yield of crude product amounts to 85% to 90% of theory, depending on the purity of the starting material. The crude product is not sufficiently stable chemically, since it contains traces of acid which cannot be removed by heating with water even with the addition of alkali. Its KI test is only a few minutes. For purification it is dissolved in hot acetone in minimum quantity, some $(NH_4)_2CO_3$ is added, and the solution is filtered on a hot water filter into twice its volume of 90% alcohol, precipitating pure pentaerythrite tetranitrate in fine needles. The yield of pure product is about 90% of the crude used and 85% of theory.

Properties of Pentaerythrite Tetranitrate. Pentaerythrite tetranitrate is a white solid, forming good crystals, melting at 138.5°C. It is insoluble in water, slightly soluble in alcohol and ether, and readily soluble in acetone. It is quite stable toward the usual heat tests, and can be stored for long periods. On heating it begins to decompose visibly at 145°C. and deflagrates at 205°C. Under the 2-kilogram weight it explodes at about 20 centimeters.

Its explosion equation may be:

$$C(CH_2NO_3)_4 \rightleftharpoons 3\ CO_2 + 2\ CO + 4\ H_2O + 2\ N_2$$

and it has, therefore, a slight oxygen deficiency. Its heat of explosion is 1,523 Calories per kilogram at constant volume with water gaseous. It has given, when compressed, a velocity of explosion as high as 8,000 meters per second, a lead-block expansion of 560 cc. for 10 grams, and it exhibits a remarkably powerful crusher test (see Chapter 16). It is an explosive of the highest order. It is also remarkably sensitive to detonation. Tetryl, which is moderately sensitive, requires 20 milligrams of $Pb(N_3)_2$ for detonation; 1 milligram is enough for P.E.T.N. The weakest blasting cap fires it with its full power. It is now being extensively used as an initiating explosive, especially in commercial rapid fuse known as Primacord, in blasting caps, and in explosive mixtures.

Discussion Questions and Exercises

1. Report on nitroglycerine as an ionizing solvent.

2. Is it wise to keep quantities of pure nitroglycerine about? Why?

3. Prepare a flow sheet for nitroglycerine; estimate the time of a cycle of operations and the material cost of producing 2,000 pounds of product.

4. Describe nitroglycerine as an explosive by the usual scheme.

5. Describe the general nature of "straight" dynamite, "special" dynamites, blasting gelatin, gelatin dynamites, permissible dynamites, and permissible gelatines.

6. Prepare outlines for the analysis of the various types of explosives enumerated in question 5.

7. Prepare a report on hexanitromannitol as an explosive.

8. Are the explosives discussed in the above exercises relatively cheap or expensive explosives?

9. Prepare a flow sheet for P.E.T.N.

10. After you have studied Chapter 6, return to this chapter and make some of the explosive calculations for the explosives listed in this chapter.

11. From Raoult's Law and the formulas and melting points, draw some freezing point curves for nitroglycerine and substances which might be mixed with it to make it nonfreezing.

12. In addition to lowering the freezing point, what other characteristics should an addition to nitroglycerine have for this purpose?

13. What other practical problem can you think of which is in several respects similar to the freezing of dynamite? Is it usually solved in the same way?

14. For further information about nitroglycerine explosives, see Chapter 17.

CHAPTER 6

Elementary Theory of Explosive Action

General Considerations. A number of the characteristics of explosives have now been mentioned. From the practical standpoint, the important characteristics are determined to some extent by the intended use. For all purposes, the power is significant. How an explosive manifests that power, whether slowly as in a propellant or rapidly as in a brisant explosive, the controlling conditions and their measurement are clearly and mutually related. In general, however, it may be said that power and sensitivity are the outstanding characteristics of explosives. Other determining conditions become pertinent as we visualize the specific use. For a military explosive, important considerations include the relative sensitivity to shock or friction that may occur during loading operations, firing of the gun, transportation, or penetration by bullets; the stability during storage involving chemical stability to temperature changes, hygroscopicity, reaction with metals and other materials with which stored explosives may be in contact; the availability and cost of raw materials; the amount of flash on discharge; the ease of firing at full power; the amount of smoke, that is, solid products of reaction—all these matters appear obvious. For industrial use, safety is also an important factor, although one normally can rely more on reasonable care; explosion temperature, toxic products, and other matters all enter in.

While it is true that any rapid change accompanied by an increase in volume may result in explosion, for example the freezing of water, most practical explosives depend upon a chemical reaction to form gases which under the initial conditions would occupy a larger volume, and hence derive their power from the pressure created by the instantaneous change. If the change moreover is exothermic—and most explosions are—the increase in heat content will raise the temperature of the gases. Thus at instantaneously constant volume the pressure is further raised and still further increases the power. The initial reacting system may have any physical state. Military and blasting explosives are more readily handled in the circumstances of their use if they are solid, and they usually are. But liquids and gases have specialized fields, in rockets for example; and explosive gases are extensively and importantly used for the generation of power in internal-combustion engines. Much of our present quantitative knowledge of the action of explosives is based upon the experimental study of explosive gas reactions, as well as much of the efficiency of the modern internal-combustion engine.

The Explosion Reaction. Let the general explosion reaction be

$$\mathrm{E} \rightleftharpoons a\,\mathrm{A} + b\,\mathrm{B} + \cdots + Q,$$

where E is any explosive material of density d, Q is the heat of reaction, and all other symbols convey the meaning of a balanced chemical equation. Assume E to be a solid, but the other reactants may have any physical state provided that at least one is gaseous. All symbols, as defined here, will be used continuously hereafter with the same meaning. Q here would be the heat of reaction for formula weights. Let n be the total number of gram molecules of gas formed for the equation as written, that is, for one gram molecule of E.

$$n = \Sigma a + b + \cdots$$

for gaseous products. For explosives Q usually has a large positive value the effect of which is to raise the system to a high temperature, known as the explosion temperature T_e, usually upwards of 1,000°C. at which water, and often other substances, are gases. Q may be measured, as we have seen, by a calorimeter experiment in which it is determined at constant pressure and all products are in their usual states, water being liquid, for example.

Here are three typical explosion reactions:

$$\underset{\text{Nitroglycerine}}{4\,\mathrm{C_3H_5(NO_3)_3}} \rightleftharpoons 12\,\mathrm{CO_2} + 10\,\mathrm{H_2O} + 6\,\mathrm{N_2} + \mathrm{O_2} \tag{1}$$

$$\underset{\text{Nitroglycol}}{\mathrm{(CH_2NO_3)_2}} \rightleftharpoons 2\,\mathrm{CO_2} + 2\,\mathrm{H_2O} + \mathrm{N_2} \tag{2}$$

$$\underset{\text{Trinitrotoluene}}{2\,\mathrm{C_7H_5(NO_2)_3}} \rightleftharpoons 12\,\mathrm{CO} + 2\,\mathrm{CH_4} + \mathrm{H_2} + 3\,\mathrm{N_2} \tag{3a}$$

$$\underset{\text{Trinitrotoluene}}{2\,\mathrm{C_7H_5(NO_2)_3}} \rightleftharpoons 12\,\mathrm{CO} + 5\,\mathrm{H_2} + 3\,\mathrm{N_2} + 2\,\mathrm{C} \tag{3b}$$

An explosive like T.N.T., which does not contain enough oxygen to oxidize completely the final products, is said to have an oxygen deficiency. One like nitroglycerine has an oxygen excess, while nitroglycol has an exact balance. This oxygen content may be expressed as a percent. Thus the complete oxidation of T.N.T. requires 33 oxygen atoms,

$$2\ C_7H_5(NO_2)_3 \rightleftharpoons 14\ CO_2 + 5\ H_2O + 3\ N_2 - 21\ O,$$

and the T.N.T. itself is lacking 21. Therefore,

$$\text{Oxygen deficiency} = \frac{21\ O}{2\ C_7H_5(NO_2)_3} \times 100$$

$$= \frac{21 \times 16}{2 \times 227} \times 100 = 74\%.$$

Similarly, nitroglycerine has a 3.5% excess. Explosives with an oxygen deficiency have a degree of uncertainty in the course of their reaction, as we see here for T.N.T. and have seen for nitrocellulose. Even with an oxygen deficiency, if the amount of oxygen present is reasonably high the explosion may be smokeless if all gases are formed, but with a large deficiency as in T.N.T., dense clouds of soot (C) may result. Oxygen deficiency represents a certain loss in explosive power, and both excess and deficiency may be compensated by compounding with other materials. T.N.T. is compounded with NH_4NO_3 to give amatol, with $NaNO_3$ as sodatol, or with other oxygen carriers. Nitroglycerine may be compounded to advantage from the purely chemical standpoint with any explosive with an oxygen deficiency.

For reaction (1), n has the value 29; for reaction (2), 5; for reaction (3a), 18; and for reaction (3b), 20.

The Gas Laws. The behavior of explosives involves to a considerable extent a discussion of the behavior of gases. Important factors in the behavior of gases are described by the Ideal Gas Law,

$$pv = nRT$$

where p is pressure, v is volume, n is the number of moles of gas, T is absolute temperature, and R is the molecular gas constant which may be taken as 0.082 liter-atmosphere or 1.985 kilogram calories. R may, however, be evaluated in any convenient units from the fact that, by Avogadro's hypothesis, and the usual chemical assumptions, one mole of an ideal gas (a gas, that is, which obeys the Ideal Gas Law) at 0°C. and 760 millimeters pressure (N.T.P.) occupies 22.41 liters.

While it is true that actual gases do not exactly obey the Ideal Gas Law, especially under the extremes of explosive conditions, it is nevertheless most often used, and the results are a first approximation, good enough for most practical purposes.

Van der Waals' equation,

$$\left(p + \frac{a}{v^2}\right)(v - b) = nRT$$

where a and b are constants characteristic of each gas, is better but too difficult for calculation. A modification,

$$p(v - b) = nRT$$

is frequently employed. b is known as the molecular "covolume" characteristic for each gas. In use, the actual value of b is usually not employed, but the assumption is often made that, for all gases involved,

$$b = \frac{M}{d},$$

where M is the mass of explosive and d its density, in appropriate units.

For ordinary purposes, from the gas laws, $v \propto \frac{1}{p}$ at constant temperature; $v \propto T$ at constant pressure; and $p \propto T$ at constant volume.

In many cases, for explosive calculations, it is assumed that changes take place without gain or loss of heat, that is to say adiabatically. Adiabatic compression, for example, results in a rise in temperature, and expansion results in cooling. For such changes we have,

$$v \propto \frac{1}{p^{\frac{1}{\gamma}}}, \qquad v \propto \frac{1}{T^{\frac{1}{\gamma - 1}}}, \qquad p \propto T^{\frac{\gamma}{\gamma - 1}},$$

where γ is the ratio of the specific heat of a gas at constant pressure and volume respectively. That is, by definition, $\gamma = \frac{c_p}{c_v}$, and it is true that for one mole of all gases, $c_p - c_v = R$.

The Heat of Explosion. In addition to calorimeter determination, the value Q may be computed from thermochemical data. It is obvious that the heat of explosion is the difference (algebraic) between the heats of formation of the final products and the heat of formation of the explosive for the equation weights. That is, if H_X is the heat of formation of substance X,

$$Q = \Sigma(a\,H_A + b\,H_B + \cdots) - H_E.$$

Heats of formation of organic compounds in general are obtained by calculation from the heat of combustion. Heats of combustion can be obtained from any handbook, but Tables 19 and 20 give some frequently used values of both.

TABLE 19

HEATS OF COMBUSTION (constant p, 15°C.)

Substance	Cal. per mole	Substance	Cal. per mole
p-aminoazobenzene	1,574	Glycerine	397
Aniline	812	n-heptane	1,150
Dimethyl-	1,143	Methyl alcohol	171
Anthracene	1,700	Mannitol	728
Benzene	782	Naphthalene	1,233
Benzyl alcohol	894	n-octane	1,303
n-butyl alcohol	639	Phenol	732
o-cresol liquid	883	Starch	4,179
m-cresol liquid	881	Sucrose	1,350
p-cresol liquid	883	Toluene	934
Diphenyl	1,494	o-xylene	1,092
Ethyl alcohol	328	m-xylene	1,088
Fructose	676	p-xylene	1,089
Glucose	673		

It is sometimes useful to compute the heat of formation of the explosive similarly first; thus, for nitroglycerine,

$$C_3H_5(OH)_3 + 3\ HNO_3 \rightleftharpoons C_3H_5(NO_3)_3 + 3\ H_2O$$

$$\begin{aligned} H_{\text{nitroglycerine}} &= H_{\text{glycerine}} + 3\,H_{HNO_3} - 3\,H_{H_2O\ \text{liq.}} \\ &= 159.3 + 3 \times 42.4 - 3 \times 68.4 \\ &= 81.3 \text{ Calories per mole.} \end{aligned}$$

The values of heat of formation, as caloremetrically measured, and given in most tables, are at constant pressure, hence Q as here calculated is the heat at constant pressure (and at 15°C., but the temperature of determination may be neglected for rough work). The first important assumption for the explosive reaction is that the products at the instant of formation occupy the volume of the initial explosive material, so the heat liberated is that at constant volume, which is greater than if the products are allowed to expand and do work on the surroundings.

TABLE 20

HEATS OF FORMATION

Substance	Cal. per mole	Substance	Cal. per mole
CO	26.43	P_2O_5	366
CO_2	94.39	KCl	104
H_2O liquid	68.39	C_2H_2	−54.34
H_2O gas	57.83	$H_2C_2O_4$	197
SO_2	69.3	NH_4NO_3	87.93
HNO_3 aq. soln.	49.8	$NaNO_3$	112
HNO_3 liquid	42.4	KNO_3	119
H_2SO_4 liquid	207.5	$KClO_3$	89.9
CaO	156	$Pb(CNS)_2$	−28.67
HN_3	−54.48	Sb_2S_3	35.84
H_2S	5.26	K_2S	88
$Hg(ONC)_2$	−64.52		

But from the gas laws, $Q_v = Q_p + 0.572\,n$. In making an actual calculation, remember to distinguish between the heat of formation for liquid (68.4 Calories) and gaseous (57.8 Calories) water.

Thus, for nitroglycerine, taking the equation above (p. 99), from which $n = 29$ for water gaseous and $n = 19$ for water liquid, and taking the heats of formation from the table, then for water gaseous,

$$Q_p = (12 \times 94.4 + 10 \times 57.8) - 4 \times 85.3;^{1} \qquad \text{(a)}$$

for water liquid,

$$Q_p = (12 \times 94.4 + 10 \times 68.4) - 4 \times 85.3.^{2} \qquad \text{(b)}$$

For (a) $\qquad Q_p = 1{,}379.6$ Calories.

For (b) $\qquad Q_p = 1{,}485.6$ Calories.

For (a) $\quad Q_v = 1{,}379.6 + 0.572 \times 29 = 1{,}396$ Calories.

For (b) $\quad Q_v = 1{,}485.6 + 0.572 \times 19 = 1{,}497$ Calories.

[1, 2] These are commonly accepted values for $-H_{\text{nitroglycerine}}$.

These values for practical purposes are usually given for 1 kilogram of explosive instead of for the equation or formula weight. The value of n under these circumstances will be called n_1. Since the molecular weight of nitroglycerine is 227, then for water gaseous,

$$Q_v = \frac{1{,}396 \times 1{,}000}{4 \times 227} = 1{,}538 \text{ Calories per kilogram,}$$

and for water liquid,

$$Q_v = \frac{1{,}497 \times 1{,}000}{4 \times 227} = 1{,}649 \text{ Calories per kilogram.}$$

The Temperature of Explosion. The temperature of explosion, in many important cases, cannot yet be precisely estimated experimentally, nor computed with any degree of accuracy. The figures of accepted authorities sometimes differ by more than 1,000°C. If T_0 be the initial temperature and ΔT be the temperature rise produced by the explosive reaction, it would appear that:

$$\Delta T = \frac{Q_v}{\Sigma(a\ c_{v_A} + b\ c_{v_B} + \cdot\cdot\cdot)} \qquad \text{(a)}$$

where the denominator is the sum of the heat capacities for all the final substances (including solids), and

$$T_e = T_0 + \Delta T \qquad \text{(b)}$$

This calculation can be made from available data as in Table 21. If done it yields results which are about 100% too high as judged by accepted values. One large source of error lies in assuming that c_v, which is usually determined at ordinary temperatures, is the same at the temperatures up to the temperature of explosion. A correction can be made by estimating an average value for each substance, as is sometimes done in practice for all the products of a given explosive. Because of the inaccuracy of the calculation T_0, if at all usual, can be neglected in equation (b).

Mallard and Le Chatelier employ in this connection the empiric equation:

$$c_{v\,\text{average}} = c_v^{0^\circ\text{C.}} + \Delta c_{v\,\text{average}} T_e.$$

Table 21 presents values of $c_v^{0^\circ\text{C.}}$ and $\Delta c_{v\,\text{average}}$ per Centigrade degree. If the value of Q_v used is based on some other temperature as it

TABLE 21

VALUES FOR THE MALLARD-LE CHATELIER EQUATION*

Gas	$c_v^{0°C.}$	$\Delta c_{v\,\text{average}}$ (small calories, per mole)
H_2	4.87	0.00082
O_2	4.98	0.00086
N_2	4.86	0.00086
H_2O	6.58	0.0029
CO	4.84	0.00086
CO_2	6.24	0.0030
NO	4.99	0.00086
NH_3	6.73	0.0060
CH_4	7.23	0.013
H_2S	6.54	0.0023
SO_2	8.14	0.024

* Additional values may be computed from data on gases given in most good handbooks; for example, the *Chemical Rubber Handbook*. These will be accurate enough for ordinary uses.

usually is, as for example 15°C., it must be converted to 0°C., and also used in small calories (= 1,000 times the number of large Calories), thus

$$Q_v^{0°C.} = 1{,}000\ Q_v^{15°C.} + 15\ (c_v^{0°C.} + 15\Delta c_{v\ \text{average}})$$

The total heat obtained by cooling the gases from T_e to 0°C. is given by $(c_v^{0°.C} + \Delta c_{v\ \text{average}} T_e)T_e$, and, since heating the gases to T_e is what Q_v does,

TABLE 22

SPECIFIC HEATS OF SOLIDS

Small calories per gram

Substance	Specific Heat
$CaCO_3$	0.203
$(NH_4)_2SO_4$	0.337
NaCl	0.204
$MgCO_3$	0.200
Kieselguhr	0.188
Na_2SO_4	0.202
K_2S	0.200

$$T_e(c_v^{0°\text{C.}} + \Delta c_{v\,\text{average}} T_e) = 1{,}000\, Q_v^{15°\text{C.}} + 15(c_v^{0°\text{C.}} + 15\Delta c_{v\,\text{average}}),$$

or

$$T_e = \frac{-c_v^{0°\text{C.}} + \sqrt{4{,}000\Delta c_{v\,\text{average}} Q_v^{15°\text{C.}} + (c_v^{0°\text{C.}} + 30\Delta c_{v\,\text{average}})^2}}{2\Delta c_{v\,\text{average}}}$$

In making a calculation it is better to calculate the value of c_v as a total for all the products of the reaction rather than for each individual one. If one of the products is solid, its specific heat is included in $c_v^{0°\text{C.}}$ and neglected for $\Delta c_{v\,\text{average}}$, which merely involves assuming the temperature coefficient for a solid to be 0, which is not a large error.

EXAMPLE: Calculate the explosion temperature of normal heptane and oxygen, given that

$$C_7H_{16} + 11\ O_2 \rightleftharpoons 7\ CO_2 + 8\ H_2O.$$

From Table 21 and by the earlier calculation we find:

$$Q_v^{15°\text{C.}} = 1{,}239 \text{ Calories,}$$

$$c_v^{0°\text{C.}} = 7 \times 6.24 + 8 \times 6.58 = 96.32$$

$$c_{v\,\text{average}} = 7 \times .003 + 8 \times .0029 = .0442$$

Hence:

$$T_e = \frac{-96.32 + \sqrt{4{,}000 \times 1239 \times .0442 + (96.32 + 30 \times .0442)^2}}{2 \times .0442}$$

$$= 4{,}087°\text{C.}$$

It is evident that if any inert material be mixed with an explosive, since its heat capacity will utilize some of the heat of explosion without contributing to it, the result will be to lower the temperature of explosion. (There is also a loss of power.) Application of this fact is made in the production of permissible explosives and flashless propellants. Sodium chloride, ammonium chloride, ammonium oxalate, various hydrates, calcium carbonate, and other materials may be used. If the substance dissociates chemically the heat absorption may be relatively large. If the substance vaporizes or dissociates into gaseous products, it may partially compensate for the power loss.

The Specific Pressure. When an explosive is fired there is a sudden increase in pressure which is due, in terms of our assumptions, chiefly to (1) the liberation of large quantities of gas, and (2) the expansion of the gases because of the rise in temperature. This pressure increase is the source of the power of the explosive. It can be expressed in a variety of ways, but conventionally usually is given as the "specific pressure" (f). The specific pressure f is defined as the pressure in appropriate units exerted by 1 kilogram of explosive in a volume of 1 liter at the explosion temperature T_e. The quantity of explosive, 1 kilogram per liter, is defined as a "loading density" of 1, (designated by the symbol Δ). Loading density is a quantity similar in some respects to other densities, and may be similarly treated. In the English, as opposed to the metric system, loading density is often defined as the ratio of the weight of explosive to the weight of water necessary to fill the volume which it occupies. This definition makes loading density a constant for a given case in both systems of units.

For any explosive reaction, taking n_1 as previously defined (number of moles of gases formed from 1 kilogram of explosive), the gases would occupy 22.41 n_1 liters at N.T.P. Since one atmosphere pressure is 1.033 kilograms per square centimeter, then at a loading density of 1,

$$p^{0^\circ\text{C.}} = 1.033 \times 22.41\, n_1 \text{ kilograms per square centimeter,}$$

and by the gas laws

$$f = 1.033 \times 22.41\, n_1 \left(\frac{273 + T_e}{273}\right)$$

$$= 0.08476\, n_1\, (273 + T_e) \text{ kilograms per square centimeter.} \quad \text{(A)}$$

Since this pressure is relatively high the Ideal Gas Laws do not apply too well. (What other equation already given would be better?) Using the covolume as a correction, a correction factor of

$$\frac{1}{1 - \dfrac{\Delta}{d}}$$

may be employed to raise the pressure in this ratio, based on the previous assumption. Or the covolume may be estimated as $\frac{1}{1000}$ of the volume of the gases, which gives the factor:

$$\frac{1}{1 - \dfrac{n_1 \times 22.41}{1{,}000}\Delta}$$

It is obvious that the actual pressure should vary directly as the loading density. The pressures actually exerted by explosives may be measured by a variety of gauges, some of which will be described later, and in general are greater than this expression predicts, particularly at loading densities of 1 and higher.

EXAMPLE: Calculate the specific pressure for nitroglycerine, given that

$$4\ C_3H_5(NO_3)_3 \rightleftharpoons 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

$$n_1 = \frac{29 \times 1{,}000}{4 \times 227} = 31.94.$$

Taking T_e for nitroglycerine as 3,360°C.,

$$f = 0.08476 \times 31.94 \times 3{,}633$$

$$= 9{,}840 \text{ kilograms per square centimeter.}$$

Velocity of Explosion. As has been emphasized, the velocity of explosion is an important factor in explosive behavior. Velocities may also be computed approximately from other experimental data, and their measurement has been described. Velocities under 1,000 meters per second are usually those of low explosives, and velocities above that figure are characterized by striking, *brisant*, or high-explosive effects. The velocity varies with a variety of factors: temperature, pressure, mode of initiation, degree of compression, density, and—very importantly—physical form of the explosive (as powder or solid mass). There are empiric equations for some of these variations, but for practical purposes one usually selects the experimental value for the substance in question as available in some table which seems to approximate his circumstances; lacking such tables, one must make a determination. Rise in temperature, pressure within limits, and increase in density usually increase velocity.

Work Performed by an Explosive. No theoretical expression as yet developed is a good measure of the practical performance of an explosive under all conditions. For practical uses of all kinds, as will be seen in greater detail in Chapter 17, the usual procedure is to study the action in practice and to set up empiric equations based on these experiences, with large margins of correction. Actual weights of charges to be used are found in this way.

Some bases for comparison can be established by the use of certain arbitrary laboratory tests which have become standardized. These will be more carefully described elsewhere (Chapter 16), but they should be enumerated here:

(1) Trautzl block test, or lead-block expansion.
(2) Hess crusher test, or small lead-block test.
(3) Ballistic mortar.
(4) Ballistic pendulum.
(5) Sand test.

Tests 1, 2, and 5 are essentially tests for *brisant* explosives and with low explosives yield results either of zero, or so low as to make comparisons meaningless. Table 44 (later) gives some typical figures. Even for high explosives, these values vary widely and comparisons between different explosives are sometimes uncertain. The figures obtained by these tests for different weights of the same explosive do not bear any easily calculated relation to each other, and it is usual to employ always the same weight of explosive for the same test, as 10 grams in the Trautzl block test, or 50 grams in the Hess crusher test.

The total work which an explosive is capable of doing is given by Q_v, even though under a given set of actual conditions the explosive may not do it. This total capacity for work is sometimes expressed in units of mechanical energy and known as the "potential" of the explosive.

$$\text{potential} = 425\, Q_v \text{ kilogram-meters}$$

where 425 is the mechanical equivalent of heat in these units.

The "characteristic product" (C.P.) is a similar quantity, which is defined as the product of the heat of explosion and the specific volume of the gases formed.

$$\text{characteristic product} = 22.41\, n_1 \left(\frac{273 + T_e}{273}\right) Q_v$$

The actual work done is very clearly related to the velocity of detonation in practice, and many expressions including it have been proposed, the general thought being that the energy of explosion is a kind of kinetic energy in which there is some correspondence between specific pressure and velocity of detonation and the usual terms of kinetic energy of motion. Some of these expressions are:

(1) The work done by the explosive in unit time, that is its power, P, varies:

$$P \propto \frac{\text{characteristic product}}{\text{time of explosion}}$$

where the time of explosion is calculated from the experimentally determined velocity of explosion.

(2) The total work done by the explosive (W) is given by:

$$W \propto \frac{mV^2}{2}$$

where m is the mass of explosive in kilograms, and V is the velocity of detonation.

(3) Also, $W \propto f \times d \times V$

where the symbols have the meanings already defined.

These expressions are essentially measures of *brisance* and may be compared with the results of experiments designed to estimate *brisant* effects. None of them agree too well with experimental results. It should also be borne in mind that all of the calculations of this chapter are highly simplified procedures which yield at the best only first approximations. They are nevertheless satisfactory for many purposes, practical and otherwise. Careful computation of the behavior of explosive substances is one of the most difficult, involved, and interesting problems of modern chemical thermodynamics.

Propellants and Internal Ballistics. For one use of explosives it is possible and desirable easily to make some fairly exact computations —the use in propelling a projectile from a gun. If an explosive be chosen at random and fired under conditions where it might be expected to expel a projectile, several things may happen. The projectile may or may not be ejected at varying speeds, and the gun may or may not explode. By proper design, a gun which will not explode for a suitable weight of explosive may be obtained. Under these circumstances some explosives will expel the projectile at high velocities and some, which may be just as powerful, will not. The difference will then be determined by velocity of explosion, and explosives with high velocities prove unsatisfactory.

Further, when an explosive is employed to fire a projectile, it is usually desired to hit a target. The fixing of the mathematical characteristics of the path of the projectile after it leaves the gun is the problem of external ballistics. But before it leaves the gun with the last positively accelerating velocity it ordinarily will have, a number of very important things have happened and their mathematical evaluation is the problem of internal ballistics. Internal ballistics has some chemical aspects and we shall give it attention, whereas external ballistics is substantially a physical problem.

In a gun, when the charge is fired, the gas pressure immediately begins to rise in the powder chamber. The projectile at first remains stationary because it is held in place by the driving band, but beyond a certain pressure the driving band is engraved, and the projectile begins to move forward in the bore. This movement tends to relieve the pressure by increasing the volume with which the gases may expand. But the burning of the charge is not instantaneous, and the powder continues to burn and evolve gases as the projectile moves. If the burning of the powder is such that it tends to increase the pressure as it burns, it is said to be progressive burning; if the reverse, degressive burning; or it may be neither and be neutral burning. This quality of the explosive charge is largely determined by grain shape and size (Chapter 7). However, as long as the projectile is in the bore it is acted upon by a fairly high pressure which reaches a maximum at some point between its original position and the muzzle, and functions as an accelerating force. The point in the bore at which the projectile is driven by maximum pressure is determined by a number of factors such as the size of the charge and the design of the gun (which must naturally be designed to withstand all the pressure to which it is subjected); in many guns this point is about a foot in advance of the powder chamber. The problem of interior ballistics is to fix the variables and functions of this situation.

The Fundamental Equation. The symbols employed are defined as follows: w = mass of charge; $T_e' = T_c + 273$ = absolute temperature of explosion gases; c_v = mean specific heat of all explosion gases at constant volume; J = mechanical equivalent of heat.

And, at the end of any time t, z = fraction of charge burnt, T = mean absolute temperature of the gases, and W = amount of external work done.

It may then be readily shown that

$$W = Jwzc_v(T_e' - T) \qquad (1)$$

And if c_p = mean specific heat of the gases at constant pressure, then [refer to (A), p. 107, and previously]:

$$J(c_p - c_v) = R = \frac{p_{0^\circ\text{C.}}\, v_{0^\circ\text{C.}}}{273} = \frac{f}{T_0}$$

where f is, as before, specific pressure, and R must be evaluated for 1 kilogram of explosive ($v_{0^\circ\text{C.}}$ and $p_{0^\circ\text{C.}}$ are at N.T.P.).

Now let V_0 = cubic capacity of the powder chamber of the gun, Ω = cross-sectional area of the bore, x = distance the projectile moves along the bore in time t, d = specific gravity of the propellant, V_t = volume occupied by gases at time t.

Then, using the gas law form $p(v - b) = nRT$, and assuming $b = \frac{\text{M}}{d}$ (which eliminates a fundamental explosives constant usually appearing in the resulting equation, and designated by η)

$$V_t = V_0 + \Omega x - \frac{w}{d}(1 - z) \qquad (2)$$

Now let m = mass of projectile, corrected as below; u = velocity of projectile, that is $\frac{dx}{dt}$; $\gamma = \frac{c_p}{c_v}$.

From (2) and the other equations and assumptions given, there may be derived,

$$fwz - p\left(V_0 + \Omega x - \frac{w}{d}\right) = \tfrac{1}{2}(\gamma - 1)mu^2 \qquad (1)$$

This equality is known as the fundamental equation of motion of the projectile. In practice, various factors introduce discrepancies which may be corrected by modifying the values of f, m, and γ.

The Dynamic Equation. From Newton's Second Law,

$$\Omega p = m\frac{du}{dt} = mu\frac{du}{dx}, \qquad (\text{II})$$

since

$$u = \frac{dx}{dt}.$$

Combustion of the Propellant. The final equations we require for the solution of problems relate to the burning of the charge. These equations can be derived by assuming that:

(1) All of the charge is ignited at once, a condition which it is desirable to approach closely in practice by proper design.

(2) The burning of each grain of charge occurs in parallel layers normal to the surface of the grain (Piobert's Law).

(3) The rate of burning of the charge along a normal to the surface of the grain is proportional to some power of the pressure (Vieille's Law).

These assumptions have some experimental support, and from them can be obtained equations IIIa and IIIb, and III given in Chapter 7 (page 122).

Solution of the Equations. Any related problem may now be approached by solving equations I, II, IIIa, and IIIb, or I, II, and III considered as simultaneous equations. To obtain a numerical solution in a particular case it is necessary to know: (1) All of the numerical values related to the gun, charge, and projectile except the one to be computed. These are fixed by the facts of the situation in question. (2) The constants for the explosive being used, f, w, n in p^n, (and η which we eliminated, for the exact general case). These facts may be determined experimentally or in some cases calculated as we have seen. The measurement of explosion-pressure variation with time is difficult and will be referred to later. γ is readily determined at ordinary temperatures, or calculated theoretically, but at the temperatures of explosion it is difficult to measure, and has to be approximated in various ways. The value for cordite is often taken as 1.2.

These equations are differential equations. The initial conditions are those necessary to engrave the driving band of the projectile, for which the pressure required may be calculated or determined experimentally. On solution, they yield, with the proper conditions, fairly exact answers to any given problem. But their exact analytical solution is a difficult problem mathematically and in practice the answers are usually found by the use of tables of interior ballistics.[3] In specific problems, however, the solution can often be expedited by making simplifying, approximate assumptions; for example, it can sometimes be assumed that $z = 1$, when the projectile leaves the muzzle, without too great error.

The Le Duc Equations. In the actual use of guns, the determinations of weight of charge, muzzle velocities, and maximum pressures generated are the most important. All of these are determined experimentally—muzzle velocities by the use of chronographs and pressure by pressure gauges in range firing, using known weights of charge. Captain A. Le Duc of the French artillery devised some empiric equations, based on his knowledge and experience, which are now universally used. These enable some problems to be solved with greater facility than with the preceding equations, although not with the same degree of exactness. Le Duc employs the equations,

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[3] U. S. Ordnance Dept., Doc. #2039, *Tables for Interior Ballistics.*

$$U = \frac{a_1 X}{a_2 + X},$$

$$a_1 = 6{,}823\left(\frac{w}{m}\right)^{1/2}\Delta^{1/12},$$

and

$$a_2 = \beta\left(1 - \frac{\Delta}{d}\right)\left(\frac{V_0}{m}\right)^{2/3},$$

where U is the muzzle velocity, X is the length of the bore, and the other symbols have the meanings already defined. As given, the units are intended to be English system with V_0 in cubic inches, and velocities in feet per second. β is a new (for us) explosive constant (the "powder constant") which for a given explosive is first determined by firing a given gun with known characteristics, and a known weight of charge, and measuring the muzzle velocity. Thus for straight nitrocellulose powder, β may be taken as 0.5315.

Example: Given a 12-inch gun using straight smokeless powder, which has a powder chamber of 4,200 cubic inches, bore 50 feet in length, charge weighing 220 pounds, projectile weighing 700 pounds, powder of specific gravity 1.61. Calculate the muzzle velocity of the projectile.

$$U = \frac{a_1 \times 50}{a_2 + 50}$$

$$a_1 = 6{,}823\left(\frac{220}{700}\right)^{1/2}\left(\frac{220}{\frac{4{,}200}{1{,}728} \times 62.5}\right)^{1/12} = 3{,}963$$

$$a_2 = .5315\left[1 - \frac{\frac{220}{\frac{4{,}200}{1{,}728} \times 62.5}}{1.61}\right]\left(\frac{4{,}200}{700}\right)^{2/3} = .18$$

$$U = \frac{3{,}963 \times 50}{.18 + 50} = 3{,}950 \text{ feet per second.}$$

Muzzle velocity varies with temperature, and 70°F. is assumed or a correction must be made. From the Le Duc equations the maximum pressure occurring, producing velocity only, is given by:

$$P_{\text{Max.}} = \frac{4w\,a_1^2}{27g\Omega a_2},$$

where g is the gravitational acceleration (= 32 feet per second per second) and all are as before in English units. The actual bore pressure, because of friction and other energy besides translation furnished, is about 12% greater than this maximum, and likewise for all other pressures calculated in this way.

Summary. We have now discussed some of the principal points in the theoretical behavior of explosives. Some other aspects, such as sensitivity, should really be treated here, but will be covered in connection with initiators and their action. The variation of some of the properties with changes in other factors will be to some extent treated also in later places.

At various points in the text and in the Appendix, in addition to the tables given here, representative values of these quantities are given. For various guns, the weight of projectile may vary from a few grams to 2,500 pounds, the weight of powder charge from a few grams to 1,000 pounds, and muzzle velocities from 600 to 4,000 feet per second. In general, for large guns, the powder charge is about one-third of the weight of the projectile and a representative muzzle velocity is 2,500 feet per second.

A point worthy of notice is that the force of explosion of the propelling powder is exerted equally upon the projectile and upon the gun in terms of Newton's Law of Action and Reaction. The backward acceleration of the gun, proportionally to its weight, is nearly the same as that of the projectile, and results in the phenomenon of recoil. Energy of recoil is made use of in many features of gun design, including automatic firing.

Discussion Questions and Exercises

1. In practicing the calculations of this chapter, bear in mind the explosive substances carefully treated in this volume: black powder,

nitrocellulose, nitrostarch, nitroglycerine, pentaerythrite tetranitrate, NH_4NO_3, tetryl, picric acid, ammonium picrate, lead azide, and fulminate of mercury; and their useful practical forms.

2. List as many of the properties of explosives which are of practical importance as you can at this point.

3. Calculate the exact oxygen balance for all the explosives in question 1.

4. Tabulate the values of γ at two temperatures for all gases in Table 21.

5. What practical effects of adiabatic compression are you familiar with?

6. Tabulate the values of Q_v which you calculate for the pure substances in question 1.

7. What is Q_v for 75% guhr dynamite? If the 25% of guhr was replaced by sawdust, what would be the effect on Q_v? Figuring the sawdust as carbon to make the computation simpler, what is the composition of the mixture which has the maximum Q_v?

8. Calculate T_e for the explosives in question 1. Make the computation for one on the basis of specific heat alone, and compare.

9. Calculate T_e for 75% guhr dynamite.

10. Calculate T_e for 50–50 amatol.

11. Calculate T_e for the maximum mixture in question 7.

12. Calculate the specific pressures for all the explosives in question 1. For any one make the covolume correction by both methods and note the percentage change.

13. Find and tabulate the velocities of explosion for the explosives in question 1.

14. Calculate and tabulate, for the explosives in question 1: (a) potential; (b) characteristic product; (c) power; (d) total work, by both methods, in the same units.

15. Calculate the maximum pressure attained in the example on p. 114.

16. Obtain the corresponding data for other guns and make calculations of muzzle velocities.

17. In the example on p. 114, what weight of charge would be necessary to give a muzzle velocity of 2,000 feet per second.

18. In the example on p. 114 make a graph for the variation in muzzle velocity with weight of charge; with length of bore.

19. Does all the energy of the propellant furnish acceleration only for the projectile?

20. Make the calculations of this chapter for the nitroglycerine explosives listed by composition in Table 16.

21. Using the tables given, and the following equations, calculate the explosives constants for pyrocellulose:

$$C_6H_{12}O_6 + 6\ O_2 \rightleftharpoons 6\ CO_2 + 6\ H_2O + 673{,}000 \text{ calories}$$

$$4\ C_6H_{12}O_6 + 11\ HNO_3\ (aq.) \rightleftharpoons C_{24}H_{29}O_9\ (NO_3)_{11} + 15\ H_2O$$

$$2\ C_{24}H_{29}O_9\ (NO_3)_{11} \rightleftharpoons 41\ CO + 7\ CO_2 + 29\ H_2O + 11\ N_2.$$

22. The "Big Bertha" with which the Germans shelled Paris during the First World War had a maximum range of about 80 miles and the following characteristics: length of bore, 105 feet; caliber, 8.4 inches; weight of projectile, 232 pounds; weight of charge, 432 pounds. The powder chamber was about 10.5 feet long and may have had a capacity of about 20,000 cubic inches. Calculate the muzzle velocity and maximum pressure, using straight smokeless powder for which $\beta = 0.5315$ and $d = 1.61$. These values are said to have been 5,400 feet per second and 63,000 pounds per square inch, in actual use, as the gun was designed.

23. Calculate muzzle velocity and maximum pressure in these cases:

	I	II
Length of bore, feet	6.21	9.59
Caliber, inches	3	4.7
Weight of projectile, pounds	14.98	45
Weight of charge, pounds	1.355	2.46
Powder chamber, cubic inches	66.5	251

25. In any of the preceding examples calculate the change in charge necessary to produce higher or lower muzzle velocities, and also the accompanying changes in pressure.

26. Based on the energy content of the propellant and the velocity of the projectile, calculate the efficiency of any given gun.

CHAPTER 7

Grain Size and Shape

Introductory. In the case of any explosive whose action is designed to be chiefly propellent, and consists of ignition and burning, the size, shape, and uniformity of the particles of which it is composed will make a considerable difference in its behavior. The same thing is true for a high explosive. The matter is not in general of as great importance with high explosives as with propellants, although the velocity of detonation is greatly affected especially by volume density as related to it. The phenomenon was noticed in the earliest days of gunpowder, which after 1600 ceased to be a powder and was granular in its final form. In general, the larger the grain the slower is the rate of burning, and there is a consequent corresponding change in the rate of development of pressure. In this connection it is to be noted that "grain" means one particle of powder regardless of size. One grain of smokeless powder for a 16-inch cannon weighs about 40 grams.

General T. J. Rodman[1] of the United States Army was the pioneer in investigating the phenomenon carefully for gunpowder and invented the multiperforated grain which is now standard. His results have been greatly expanded and extended to all kinds of propellent powders.

Laws of Burning. For calculation, the assumption is usually made that all particles of a propellent charge are ignited simultaneously. In practice, it is a matter of great importance that the igniting device be of such size and design that this condition shall be as nearly fulfilled as possible.

Limiting consideration for the moment to the behavior of a single grain, it is clear that ignition takes place on the surface. Piobert's Law (1840) states that the combustion of a grain takes place in parallel layers, perpendicular to a normal to the surface at any point.

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[1] T. J. Rodman, *Experiments on Metal for Cannon and Qualities of Cannon Powder.*

It is clear that any solid grain of any ordinary shape, even though irregular, will burn with a constantly diminishing surface, and therefore regularly decreasing rate of evolution of gas and pressure. A powder of that character is said to be *degressive* burning. Consider a powder of cylindrical grains with one cylindrical perforation down the center (Figure 9). Such a grain, when ignited, will have a decreasing outer surface but an increasing inner one. The two effects will nearly offset each other, and a grain of these characteristics is said to be a *neutral* grain. In the case of a cylindrical grain with more than one internal perforation, the increase in inner surface may more than equal the decrease in outer surface, in which case the powder will burn with an increasing rate of evolution of gas and pressure and is said to be *progressive* burning.

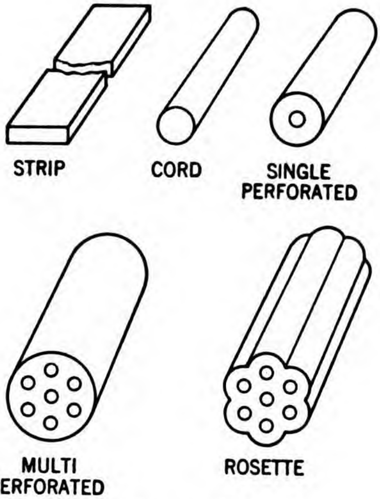


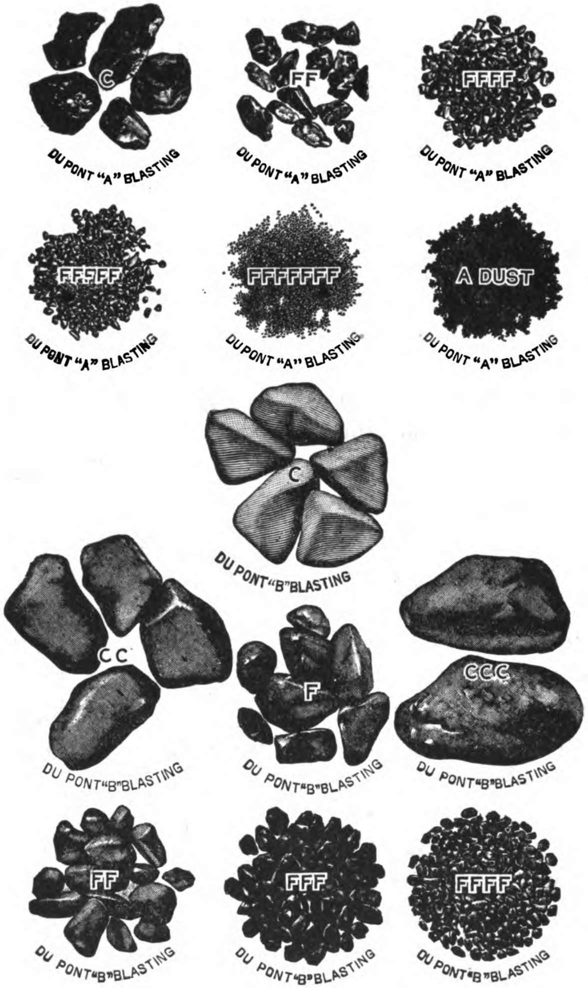
FIGURE 9
Forms of Powder Grains

Other physical factors influence the rate of burning. A grain of smokeless cannon powder when ignited by a flame (Try it! See page 22) in air burns slowly, and a large grain may take several seconds before it is consumed, whereas in a cannon several hundred pounds will be burned in a small fraction of a second. The rate of burning of the charge along a normal to the surface of the grain is proportional to some power of the pressure. This is Vieille's Law (1893).

Types of Grain. Gunpowder or black powder, smokeless powders, and propellent powders in general are made in many types of grain. Some of these types are irregular granules, spheres, cubes or square prisms, disks, flakes, strip, cord, single-perforated cylinders, multiperforated (usually 7) cylinders, and multiperforated cylindrical rosette or Walsh grains (Figures 9 and 10).

Black powder for blasting is usually of irregular granules that

KNO_3
S
C



differ in average size for the various grades, but is sometimes prepared in large single-perforated cylindrical grains which can be wrapped into sticks like dynamite. High-quality gunpowder may be in regular and uniform small spheres.

Smokeless powders are usually flake, solid cord, strip, single-perforated cylinders, or multiperforated cylinders for United States Army use. The rosette grain has some advantages but is not yet standard. Pistol powders are usually flake; long-bore small arms,

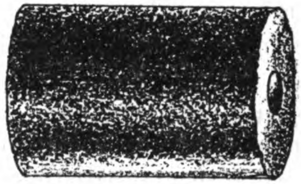


FIGURE 10

***Facing Page*—Exact Sizes of Some Black-Powder Grains; *Right*—A Single Pellet of Molded Black-Powder** (Both, courtesy of Du Pont Co.); ***Above*—A Paper-Wrapped "Stick"** (Courtesy of Atlas Powder Co.)

minor-caliber cannon, and in general guns requiring excessively thin webs use single-perforated cylinders; all large cannon use multiperforated cylindrical grains.

In general, from the standpoint of ballistics, the best form of granulation is that which meets these requirements:

(1) It will give the projectile the prescribed muzzle velocity within the permitted maximum pressure, with a minimum weight of charge.

(2) It will cause a minimum of erosion to the bore.

(3) It will show a maximum of regularity in ballistic behavior.

Slivers. Consider a multiperforated cylindrical grain such as that shown in Figure 11. When this grain is ignited and burns, it goes

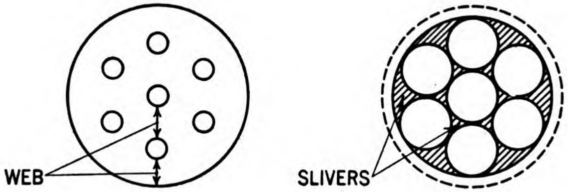


FIGURE 11: **Burning of a Multiperforated Grain**

through the stages indicated, and as the inner tubes enlarge, the grain is broken down into solid pieces of triangular cross section which are shaded in the diagram. These are known as slivers.

From the usual type of cylindrical grain with 7 perforations, 12 of these slivers are formed, which at that instant constitute about 15% of the total weight of the grain. The slivers burn degressively and are usually consumed in the bore of the weapon. If, however, the bore of the weapon is relatively short (for example, in a mortar), or if a reduced charge is fired developing a low pressure and a low rate of burning, then the slivers may be expelled unburned from the muzzle. The Walsh or rosette grain has the outer surface of the grain scooped out, roughly following the pattern of these slivers (of Figure 11), and thus reduces the amount of sliver formation by almost half (exactly half in theory), and reduces or eliminates the ejection of unburned powder from the mouth of the weapon. This improvement reduces flash and other undesirable effects and has been used in some seacoast mortars.

Vieille's Law. Consider now a burning grain of powder. Let l = the least distance along a normal to the surface of the grain for which the grain is completely consumed.

yl = the distance burned in time t.

Then, by Vieille's Law,

$$l\frac{dy}{dt} = \omega p^n, \tag{III, a}$$

where p is the pressure, and ω and n are constants characteristic of the propellent explosive used. Their experimental determination is important and was first done by Nobel. As a rule, $.5 < \omega < 1$. For practical, as opposed to theoretic purposes, the "powder constant" can be put in another form (see page 114).

If z is the fraction of the weight of powder burned in time t, it may be shown that

$$z = ay(1 - \lambda y + \sigma y^2) \tag{III, b}$$

where a, λ, and σ are constants which depend on the geometric shape of the grain, and which satisfy the condition $a(1 - \lambda + \sigma) = 1$. Table 23 gives formulas for the values of these constants for some grain shapes and they may then be computed from proper measurements of the given grains.

Equations (III, a) and (III, b) are part of the data needed for the exact solution of important problems in internal ballistics. Charbonnier devised an alternative equation to them.

Let S = surface area of the grains of the charge at time t, S_0 =

TABLE 23

VALUES OF GRAIN-SHAPE CONSTANTS

Grain shape	Basic dimensions and size	a	λ	σ
Single-perforated cylinder	Web. . . . . $2\,l$ Length. . . . . $2\,kl$	$1 + \frac{1}{k}$	$\frac{1}{1+k}$	0
Solid cylinder or square-section strip	Diameter or side. . . $2\,l$ Length. . . . . $2\,kl$	$2 + \frac{1}{k}$	$\frac{2+k}{1+2k}$	$\frac{1}{1+2k}$
Circular or square flake	Diameter or side. . . $2\,kl$ Thickness. . . . . $2\,l$	$1 + \frac{2}{k}$	$\frac{1+2k}{k(2+k)}$	$\frac{1}{k(1+k)}$

initial value of S, and C_0 = initial volume of the charge. Other symbols have their previous meanings. Then,

$$\frac{dz}{dt} = \frac{S}{C_0}\frac{dy}{dt} = \frac{S_0\omega}{C_0}\,p^n\,\theta(z) \qquad \text{III}$$

where

$$\theta(z) = \frac{S}{S_0}$$

The function $\theta(z)$ is called the function of form and depends upon the geometric shape of the grain. It is usually of the mathematical form $\sqrt{1 - bz}$, where b is a constant dependent on grain shape. With some simplifying assumptions the value of b for a tubular grain is $\frac{4k}{(1+k)^2}$; for a cord or square prism, 1; and for a disk or square flake,

$$\frac{8k}{(2+k)^2}.$$

Measurement of Grain Dimensions. From the considerations up to this point it is clear that for the solution to certain types of questions it will be necessary to measure experimentally the various aspects of grain dimensions, and also that uniformity of grains is important in the practical manufacture.

United States Standard Sieves. Where a powder consists of particles of irregular shape it is often completely satisfactory to determine the average over-all sizes on a percent-by-weight basis by sieving, using a coarse screen (the passer) and a fine screen (the duster). This obviously divides the powder into three portions of which the middle in general should be the largest.

This is usually done employing United States Standard Sieves (Figure 12). These are shallow, circular, metallic pans, 8 inches in diameter, with bottoms of standard copper or brass wire mesh, and fit into each other in nests. They can be closed with solid top and bottom pans. Table 24 shows the usual numbers and sizes.

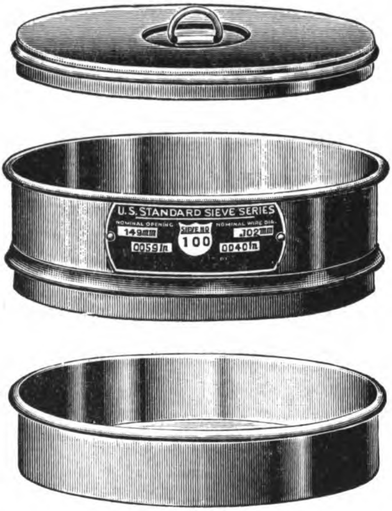


FIGURE 12: **United States Standard Sieve with Cover and Pan**
(Courtesy of Precision Scientific Co.)

TABLE 24

UNITED STATES STANDARD SIEVES

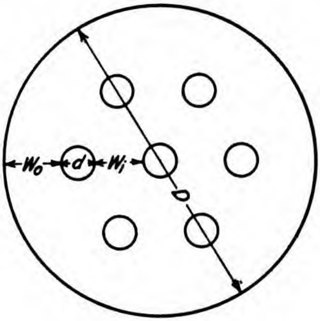
Sieve No.	Opening, mm.	Wire diameter, mm.	Sieve No.	Opening, mm.	Wire diameter, mm.
4	4.76	1.27	60	.250	.162
6	3.36	1.02	70	.210	.140
8	2.38	.84	80	.177	.119
10	2.00	.76	100	.149	.102
12	1.68	.69	120	.125	.086
16	1.19	.54	140	.105	.074
18	1.00	.48	170	.088	.063
20	.84	.42	200	.074	.053
30	.59	.33	230	.062	.046
40	.42	.25	270	.053	.041
50	.297	.188	325	.044	.036

Experiment. *Granulation of Black Powder.* Weigh out 100 grams ± 0.5 gram of sample and empty upon the prescribed passer screen. Shake vigorously over a sheet of brown paper for exactly 1 minute. Set aside the powder which has passed through the screen and empty the material remaining on the screen on to a sheet of brown paper. Strike the screen sharply with the fingers to remove any adhering powder grains. Sift the material so obtained through the same screen for exactly one minute. Empty the sieve. Remove any adhering grains and submit the material to a third similar sifting.

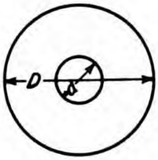
Collect the residue failing to pass the screen and weigh to the nearest tenth of a gram; from this weight, calculate the percentage of powder failing to pass the passer screen.

Empty all of the powder which has been used in the passer-screen test on to the prescribed duster screen and sift three times as just prescribed. Collect the three portions of powder passing through the screen, weigh, and calculate the percentage of material passing through the duster screen.

For many explosive materials, for example, explosive D, picric acid, T.N.T., and the like, this is a required procedure. It may also be done in one step using the passer, duster, and top and bottom cover fitted together. Experience will show that it is not a particularly accurate performance, and it is most important in securing concordant results to standardize the time and manner of shaking. Mechanical shaking is preferable but not usually prescribed. To avoid inhaling the dust is sometimes important.



CYLINDRICAL GRAIN, 7 PERFORATIONS
DRY DIMENSIONS (APPROXIMATE)
$D = 10d$
$W_o = W_i + 5\%\, W_i$
$W_a = \frac{W_o + W_i}{2}$
D = OUTSIDE DIAMETER
d = DIAMETER OF PERFORATION
W_o = OUTER WEB
W_i = INNER WEB



CYLINDRICAL GRAIN, SINGLE PERFORATION
DRY DIMENSION, $D = 3d$
D = OUTSIDE DIAMETER
d = DIAMETER OF PERFORATION

FIGURE 13
Grain Measurements

Grain Measurement. Where grains are or should be of a regular geometric shape and of a prescribed uniformity it is necessary to make actual measurements of the determining dimensions such as length, width, thickness, diameter, and diameters of perforations, if any. In the case of perforated grains the "web size" is important. By web size is meant the distance along a diameter of the grain between any two parallel surface lines. Where both such lines are inside the grain it is an inner web (W_i); where one is an external surface it is an outer web (W_o). Figure 13 is marked with the usual symbols employed. A single perforated grain has obviously only one web. By average web, in the case of a multiperforated grain, is meant the average of the inner and outer web thicknesses.

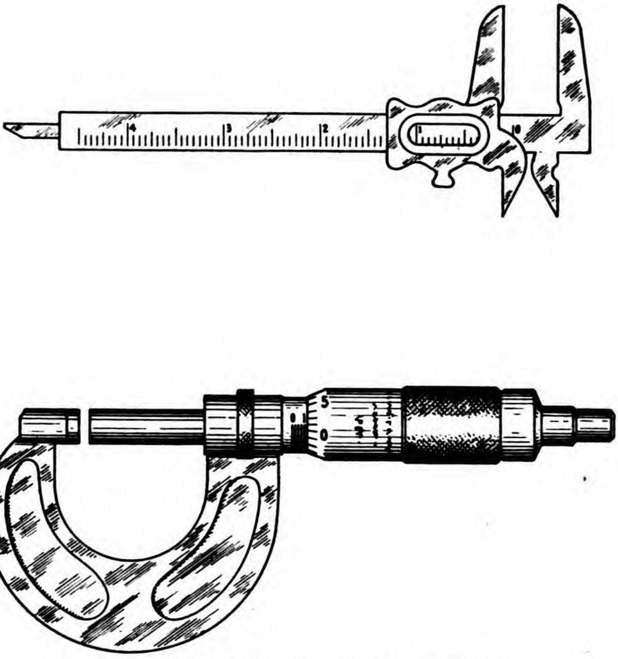


FIGURE 14: **Calipers and Micrometer**

In examining United States Army smokeless powder it is usual to measure length on 30 grains, and other dimensions on 90 grains chosen at random to be representative, and to average results. On large grains length can be measured with an ordinary caliper (Figure

14). Length of small grains, and other measurements, are made either with a micrometer (Figure 14) capable of giving measurements accurate to 0.001 inch, or with a measuring microscope. This latter is an ordinary microscope of about 25 diameters magnification equipped with an internal measuring scale, either sawtooth or cross-hair. The scale must first be calibrated against a standard stage scale graduated to appropriate units. Grain measurement is then made against the teeth or cross-hairs, estimating between them (see Figure 15).

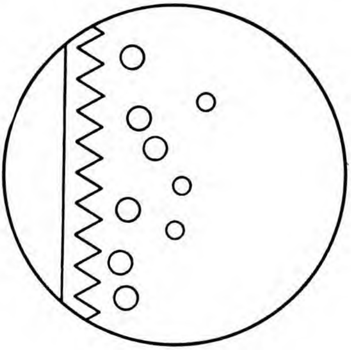


FIGURE 15

Field of the Measuring Microscope, with Gunpowder Grains

Experiment. *Grain Examination of Smokeless Powder.*

1. Determine form of grain by visual examination.

2. To determine length, select at random 30 normal grains of powder and measure the length with a micrometer. When the ends are irregular, determine the average length as closely as possible.

3. To determine grain and perforation diameters and web thicknesses, select 90 normal grains of powder; then, using a razor blade or hacksaw, cut each grain partly through from opposite sides at about the middle, and break under strain so that a narrow ridge of powder which includes the desired line of measurement is left along the line of breakage. This desired line of measurement is a straight line forming a diameter of the grain which passes through the center of the perforation of a single-perforated powder, and through the center of three perforations of a multiperforated grain.

Place a number of the grains vertically on a glass slide so that the broken ends are uppermost and the individual desired lines of measurement are in alignment. Use a film of vaseline on the glass slide to hold the grains in position if necessary. Place the slide on the stage of a measuring microscope having a magnification of about 25 diameters, equipped with cross-hairs, and having a horizontal scale and vernier screw capable of giving measurements accurate to 0.001 inch.

In the case of multiperforated grains, measure the diameter of the grain, the two outer web thicknesses, the two inner web thicknesses, and the diameters of three perforations of each of the 90 grains by means of a continuous series of readings taken along the desired line of measurement of each grain. In the case of single-perforated grains, measure the diameter of the grain, the two web thicknesses, and the diameter of the perforation of each of the 90 grains by means of a continuous series of readings taken along the desired line of measurement of each grain.

CALCULATIONS. *Length-diameter ratio.* From the measurements of length and grain diameter taken as described, calculate the ratio between the average length (L) and the average diameter (D).

Length and diameter uniformity. From the measurement of length and grain diameter taken as described, calculate the mean variation of individual dimensions from the mean dimension, expressed as percentage of the mean dimension.

Grain-diameter–perforation-diameter ratio. From the measurements taken as described, calculate the ratio between the average grain diameter (D) and the average perforation diameter (d).

Web measurements. (a) For multiperforated grains, from the measurements taken as described, calculate the average outer web thickness (W_o) and the average inner web thickness (W_i) for the 90 grains measured. Calculate the average web thickness (W_a) by taking the average of W_o and W_i. Calculate the difference between the average outer web thickness (W_o) and the average inner web thickness (W_i) in terms of percentage of the average thickness (W_a):

$$\frac{W_o - W_i}{W_a} \times 100 = \text{percentage difference.}$$

Neglect positive or negative sign.

(b) For single-perforated grain, from the measurements made as described, calculate the average of the 90 web thickness above the median and the average of the 90 web thicknesses below the median. Calculate the percentage by which each of the two averages differs from the average of all the web measurements (W_a).

$$\frac{W_a - W_{90}}{W_a} \times 100 = \text{percentage difference.}$$

Neglect positive or negative sign.

It is efficient to tabulate one's observations carefully in terms of these directions, and where many experiments are to be performed to prepare mimeographed observation sheets. The directions may be modified to include any desired measurements of any given grain.

Compressibility of Grain. When a powder is fired in a gun there is naturally a certain amount of turbulence and the grains are thrown about. Powder grains must have a certain amount of resilience or plasticity to withstand crumbling or excessive deformation under these conditions. Crumbling causes loss of grain shape, decrease in grain size, lack of uniform ballistic behavior, and possibly dangerously high pressures—it might even cause explosion of the gun. From the chemical standpoint this behavior is to some extent a function of the residual solvent in the grain, as an excessively dry grain will crumble more readily.

Experiment. *Determination of Compressibility.* In this test do not use grains which are abnormal in shape or contain obvious flaws. Cut the ends of 10 normal grains of powder so that new surfaces, perpendicular to the length, are exposed, and so that the length is equal to the diameter. Determine the average length of these pieces with a micrometer. Compress each grain between parallel surfaces, increasing the load slowly until the first crack appears. Remove the load and measure the new length of the grain. Calculate the average reduction in length as a percent of the average original length.

$$\frac{L - L'}{L} \times 100 = \text{percentage reduction.}$$

If these 10 grains fail to pass this test (see below) subject 20 more grains to the test. Calculate the percentage reduction of the total 30 grains tested.

A convenient press for this experiment, which will also be useful in loading caps for the sand test (see Chapter 16), is shown in Figure 16. The arrangement is, as indicated, for loading caps, and here the base hole may be covered by a plate. It can be built in the shop, of iron, and pressure can be sufficiently accurately estimated from the mechanical advantage. A very suitable press may, however, be made from an ordinary sodium press, by designing similar base fittings.

United States Army Specifications. At present, United States Army specifications for smokeless powder prescribe the values found in Table 25 for the properties whose measurement has just been described.

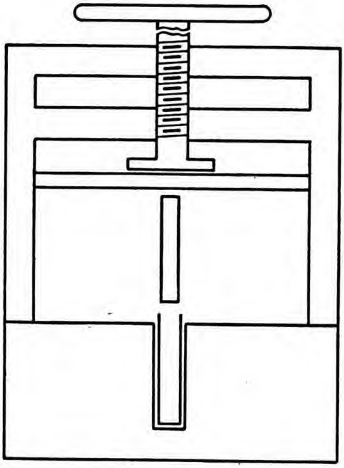


FIGURE 16

Press

Granulation of Smokeless Powder. All forms of grains described in this chapter are manufactured commercially, and many others have been or may be experimented with for research purposes. For pistols, whose performance is relatively poor ballistically, a solid grain is usually employed, commonly in the form of flakes. For long-bore small arms, and other ordnance where excessively thin webs would be required, single-perforated cylindrical grains are used because of the difficulty of making very small multiperforated cylinders. In the United States military service, the multiperforated cylindrical grain with one central perforation and six others arranged around it at the corners of a regular hexagon is standard for all large caliber guns, although the Walsh or rosette grain is sometimes used. The method of manufacturing these grains is therefore of particular interest.

TABLE 25

VALUES OF PROPERTIES OF SMOKELESS POWDERS AS PRESCRIBED BY UNITED STATES ARMY SPECIFICATIONS

Characteristic	Values	
	Multiperforated	Single-perforated
Form	7 perforations	1 perforation
L/d	2.10 to 2.50	3 to 6
L uniformity, $\frac{\Delta L}{L} \times 100$	not $> 5.0\%$ variation; desired $< 1.0\%$	same
D uniformity, $\frac{\Delta D}{D} \times 100$ $D \geq 0.2$ inch $D < 0.2$ inch	 $\leqq 2.5\%$ $\leqq 5.0\%$	 same same
D/d	5 to 15	circa 3
$\frac{W_o - W_i}{W_a} \times 100$	$\leqq 15\%$	
$\frac{W_a - W_{90}}{W_a} \times 100$		$\leqq 15\%$
Compressibility	$\geqq 35\%$	not specified

More information about grain measurements will be found in the chapter on Smokeless Powder.

Dies.[2] Figure 17 shows the general design of die through which the multiperforated powder is extruded from the graining presses during manufacture. As the powder comes from the graining press it contains from 40% to 50% solvent and is called "green" because the solvent has not been extracted by the drying processes. The green powder has about the same dimensions as the steel die through which it has just been pressed. The die body *A* consists of a steel block designed to hold the pin plate *B*, the water jacket *C* (having an inlet and outlet for water used for cooling the die while running the powder), and a closing screw *D* for the water jacket. The pin plate consists of a perforated plate to which are attached wires or pins *E*, which form the perforations in the grain, and the plug *F*, which holds the pins in place when the die is not in use. The dimensions for both the die body and pin plate are called die dimensions.

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[2] U. S. A., TM 9–2900, *Military Explosives.*

It is necessary to calculate the dimensions of the die very accurately. Many factors cause the measurements of the green powder to differ from those of the die. Among these factors is the spring of the pins (or needle wire) by which action the pins are drawn together as the powder is being pressed through the die, decreasing the inner web. Another factor is the consistency of the powder as it is being grained. The softer the powder the more it will contract as it goes through the die, thus causing the green dimensions to be less than the die dimensions.

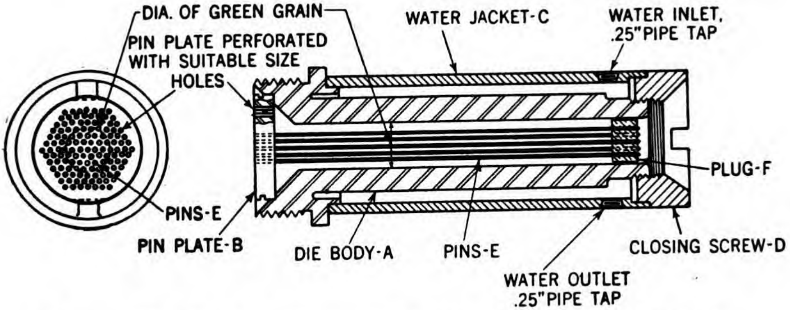
DIA. OF GREEN GRAIN
PIN PLATE PERFORATED WITH SUITABLE SIZE HOLES
WATER JACKET-C
WATER INLET, .25"PIPE TAP
PLUG-F
PINS-E
PIN PLATE-B
DIE BODY-A
PINS-E
CLOSING SCREW-D
WATER OUTLET .25"PIPE TAP

FIGURE 17: **Powder Die Assembly Used for Cylindrical Grains**

To determine the size of die required to manufacture a powder of given dry web, it is necessary to know how much the powder will shrink after the solvent has been removed. The shrinkage is expressed as the percentage reduction in a given dimension such as the web (W) from the green to the dry form. The percentage shrinkage for the various dimensions varies considerably; for example, the shrinkage in length of grain may be as small as 5%, while the web shrinkage may vary from 25% to 35%. The shrinkage for the inner web (W_i) for multiperforated powders is usually less than the shrinkage for the outer web (W_o); furthermore, the shrinkage per cent will vary considerably with composition, quantity of solvent, physical characteristics of the nitrocellulose, and size of grain. The shrinkage which occurs when the various grain sizes are manufactured according to a standardized procedure is determined by the actual manufacture of small experimental lots of the approximate grain sizes involved. Once the dry dimensions are decided upon and the shrinkage per cent known for a given composition and manufacturing procedure, the powder can be made with a reasonable assurance that it will dry closely to the size expected.

The following problem and calculations illustrate the method used for the determination of die dimensions to manufacture a powder of any given dry dimensions. Most of the symbols used in these calculations are described in Figure 14. When the symbol refers to a green dimension, it is followed by the subscript g and when it refers to the dry-powder dimension, it is followed by the subscript d.

PROBLEM. A die is desired for the manufacture of a powder of the multiperforated grain form to have an average dry web (W_{ad}) of 0.0220 inch and a dry perforation diameter (d_d) of 0.0127 inch. The shrinkages for this composition are perforation, 21.0%; outer web, 35.0%; inner web, 25%.

Solution. If we keep in mind that the pin size is equal to d_g, then

$$d_g = 0.0127 \div (100 - 21) \times 100 = 0.01606 \text{ inch.}$$

It is considered desirable to manufacture powders with outer web (W_{od}) slightly larger, usually about 5%, than the inner web (W_{id}); therefore, the outer web will be 2.5% greater than the average web or 0.02255 inch, while the inner web will be 2.5% less than the average web or 0.02155 inch.

Since it is apparent from Figure 17 that the bore diameter of the die, which is equal to the diameter of the green grain (D_g), is the sum of the thickness of the green inner and outer webs plus the diameter of the green perforations, it is necessary to determine the green dimensions of the inner and outer webs. The green outer web (W_{og}) is calculated as follows:

$$0.02255 \div (100 - 35) \times 100 = 0.0357 \text{ inch.}$$

The green inner web (W_{ig}) then is calculated similarly as 0.0287 inch. With the above data, the bore diameter (D_g) becomes 3(0.01606) + 2(0.0287) + 2(0.0347), or 0.17498 inch.

It is now necessary to calculate the diameter of the circle on which the centers of the pins must be set in the pin plate. This dimension is referred to as pin-circle diameter and is equal to $2(W_{ig}) + 2(d_g)$, which in this case is 0.0895 inch.

The length of grain or the cut remains to be determined. Since the shrinkage in length is small and since the ratio of length of grain to diameter may vary from 2.10 to 2.5, the green diameter (D_g) may be multiplied by 2.5 to obtain the length of cut. If a closer controlled length of cut is desired, the shrinkage in length must be known and the green length calculated accordingly.

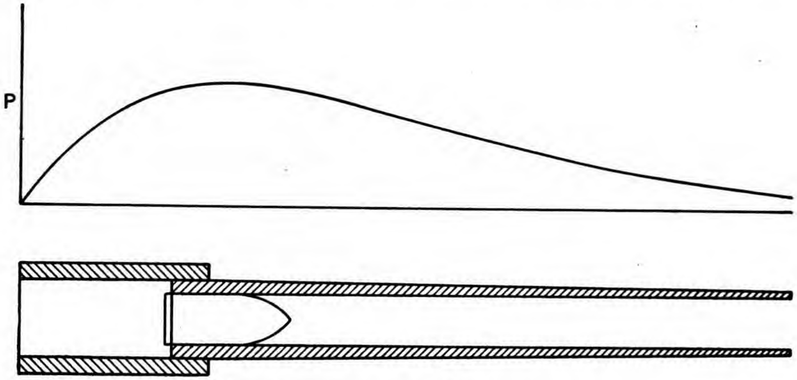

FIGURE 18: **Change in Pressure in Gun**

Behavior of a Propellent Explosive. When the propellent charge in a gun is ignited, the pressure begins to rise (see Figure 18). At a certain value, the rotating band or driving band of the projectile is engraved and the projectile begins to move forward in the bore. As it moves forward the volume allowed for the expanding gases is increased and this effect tends to reduce the pressure. As long as the projectile is in the bore the pressure is normally quite high and functions as an accelerating force on the projectile. Since it is desirable to give the projectile as high a velocity as possible, it is desirable to have the largest possible pressure acting for the full time it is in the bore. However, the design of the gun offers an upper limit; internal pressures are not allowed to exceed 45,000 pounds per square inch and usually are below 40,000.

The principal factors involved in the general situation are the total weight of the powder charge, the size and shape of the grain, the temperature attained, the length of the bore, the caliber of the gun, the weight of the projectile, the prescribed velocity of the projectile, the maximum allowable pressure, the regularity in ballistic behavior, muzzle flash, the per cent of volatiles and moisture in the powder, and the like. The design of the gun fixes many of these factors and as a rule indicates, on the basis of proper knowledge of available material, what to use. In practice, powders usually are marked for their specific use. As a theoretical problem the choice of a propellant and the calculation of the charge are much more difficult.

For example, as the weight of the projectile increases for a given muzzle velocity, other factors remaining constant, the weight of charge must be increased. But if the grain size were small the rapid burning would produce a pressure that might explode the gun. In a general way, the grain size will increase as the weight of the projectile increases.

The multiperforated grain was developed to solve, by its progressive burning characteristic, the problem of maintaining a relatively high pressure during the entire stay of the projectile in the bore, instead of having an instantaneously high and rapidly diminishing one. It is possible at present to describe the characteristics of even more desirable grains, but it is impossible to manufacture them in practice. The multiperforated grain burns to create a pressure which reaches a maximum when the projectile arrives at a point in the bore about a foot in front of the powder chamber as many guns are designed, and the progressive burning maintains a satisfactory pressure while the projectile is in the bore.

Characteristics of Weapons. Small arms include, as usually said, weapons up to a caliber of 20 millimeters. The pistol has also a very short bore as well as small caliber. Other small arms in general have relatively long bores. Guns range in length from 40 to 60 times the caliber, howitzers are relatively shorter, and mortars are relatively the shortest.

Types of Powder Required. To give the prescribed muzzle velocity for the larger guns, which is in the neighborhood of 2,500 feet per second, requires in general a powder charge of approximately one-third the weight of the projectile, although this ratio varies so widely that this generalization must not be taken too seriously (see p. 318).

As the caliber increases, the size of the powder grain may be and is increased; for small arms, relatively small grains are required which cannot be manufactured readily as multiperforated grains, and so the single-perforated cylinder is standard. In the pistol, which is relatively poor in ballistic performance, flake powder may be used.

In howitzers, where the bore is relatively short and the powder must burn rapidly, either very thin webs or a rosette grain must be used, or large quantities of unburned powder slivers will be ejected.

In a gun, as the powder-chamber capacity decreases, other factors remaining constant, the web size must decrease. For the same gun, a decrease in web size will reduce flash. An increase in the weight of the projectile requires either an increase in the powder charge or a decrease in the web size or both. The weight of powder charge may be reduced if the web size is reduced, but with considerably higher pressures. For example, in a 3-inch antiaircraft gun using a 12.7-pound projectile, the powder charge was reduced from 5.66 to 4.88 pounds by a reduction in average web thickness from 0.0444 inch to .0339 inch, but the pressure increased from 28,700 to 34,000 pounds per square inch.

In general, however, grain size, web size, and weight of powder charge increase with an increase in caliber and weight of projectile.

Effect of Moisture and Volatiles. After graining, the major part of the solvent is dried out and recovered, but from 2% to 8.5% may remain in the powder as moisture and volatiles or total volatiles, the amount depending upon the size of the grain.[3] The effect of moisture and volatiles is given by Tschappat,[4] and referred to in United States government literature as follows:

> The alcohol used in the solvent contains 5% water, which generally remains in the powder after drying. Additional water may be absorbed from the air during the process of manufacturing and handling. Recent lots of powder also contain approximately 1% of a stabilizer, and .30-caliber rifle powders contain, in addition, a small percentage of graphite.
>
> Smokeless pyro powder may, therefore, be considered to be a mixture

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[3] For specifications, see Chapter 11, "Smokeless Powder."

[4] Data slightly revised to bring up to date. Tschappat, *Ordnance and Gunnery*, p. 115.

of nitrocellulose, alcohol, water, and sometimes a stabilizer and graphite. Most of the ether used is evaporated out during the drying process.

From calculations it is found that the energy per pound of pure nitrocellulose of 12.60% nitrogen is about 1,425,000 foot-pounds per pound. If now, an inert material, that is, one that takes no part in the reaction at combustion, is mixed with the nitrocellulose, the energy per pound of the resulting material will be less than that of pure nitrocellulose. For instance, if 0.99 pounds of pure nitrocellulose of 12.60% N is mixed with 0.01 pound of inert material, the inert material will be 1% of the total weight and the energy per pound of the resulting material will evidently be 1,425,000 × 0.99 = 1,410,750 foot-pounds per pound.

Now, of the materials entering powder as given above, water is considered as having the same effect as the same percentage of inert matter. Alcohol has a greater effect than inert matter for the reason that the carbon contained in it combines with the CO_2, resulting from the combustion of the nitrocellulose, thus forming a larger quantity of CO and a smaller quantity of CO_2, than in the combustion of pure nitrocellulose. Theoretical considerations and practical tests indicate that the effect of 1% alcohol in reducing the energy per pound of nitrocellulose is equal to the effect of 2.5% inert matter.

In the same way the effect of 1% stabilizer, which is higher in carbon content than alcohol, is shown to be equal to the effect of 4% inert matter. Graphite, though entirely carbon, does not readily take part in the reaction and, therefore, the effect of 1% graphite in reducing the energy per pound of nitrocellulose is considered equal to that of 2.5% inert matter.

Consequently, the granulation of the powder must be so calculated that it will counteract the reduction of the energy of the powder by the solvent remaining after drying. In order to give more energy, the burning surface should be increased by diminishing the average web measurements or the size of the grain, or by changing the form of the grain. The quotation forms the basis for a slightly different method of calculating Q_v from that described earlier.

Discussion Questions and Exercises

1. Show, for cubes, how the total surface area of a given weight of powder increases as the size diminishes.
2. Show how, using grains of equal weights the surface area differs for the different shapes of grains.
3. Show how, using grains of approximately equal linear dimensions, the surface area varies during burning up to the instant before completion.
4. Report on the experimental determination of ω and η.
5. Prepare a sheet as suggested on p. 128 in advance of your examination of smokeless powder.

6. Tabulate and consider the actual dimensions of some typical smokeless powder grains. See Chapter 11 and make models if actual specimens are not available.

7. How does surface area affect the velocity of heterogeneous reactions in general. Is the case of powders exactly analogous? Why?

8. Solve other problems similar to the one on p. 132.

9. Based on the quotation from Tschappat, make calculations of Q_v for various smokeless powders given in Chapter 11.

10. In Figure 18, draw curves showing how you think the pressure curve differs for progressive, neutral, and degressive powders.

11. What other factors influence this curve and how?

12. Classify all of the shapes of grains described in this chapter into the classes: degressive, neutral, and progressive burning. While that is the order of increasingly better ballistic performance, what other factors may determine a practical choice?

CHAPTER 8

The Problem of Nitration

General Considerations. Most of the important large-scale explosive materials are compounds which contain one or more of the chemical groups (NO_2) or (NO_3). The problem of nitration is fundamentally that of introducing these groups into a suitable organic molecule, and the result is in general the production of compounds with explosive properties, whose power increases with the number of such groups introduced.

From the purely chemical standpoint, there are many methods by which the goal can be attained. Any process, old or new, always has potential usefulness, but at present most commercial processes involve essentially a treatment with nitric acid, according to the scheme:

$$R \cdot H + HNO_3 \rightleftharpoons R \cdot NO_2 + H_2O \qquad (a)$$

or

$$ROH + HNO_3 \rightleftharpoons R \cdot NO_3 + H_2O \qquad (b)$$

where R is any organic radical. Reaction (a) in general works for R cyclic, whereas reaction (b) takes place when OH is an alcohol group. These reactions are reversible, especially (b), which is esterification, and any device for the removal of the water formed also favors the formation of the nitrogen compound. Strong dehydrating agents therefore improve the efficiency of the reaction. While many such dehydrators may be used, strong sulphuric acid is almost always employed commercially. For practical purposes, the acids are mixed in advance, and the $HNO_3 - H_2SO_4$ mixture is known as mixed acid. Occasionally, as will be seen, the direct treatment with mixed acid is undesirable for some reason, or will even fail to yield the desired product. From the commercial standpoint, then, "nitration" means essentially the scheme, direct or indirect:

$$\text{organic substance} + \text{mixed acid} \rightleftharpoons \text{explosive} + \text{spent acid.}$$

Since the explosive produced may be either of two possible types it might be better if we had two names.

Types of Organic Substances as Starting Materials. While almost any alcohol, and any cyclic compound, as well as many other materials may be thus "nitrated," to produce explosives, explosives are materials that are to be made and used on a large scale. Therefore important practical criteria for the starting or raw materials are cheapness and availability, except for special purposes where the explosives can command a higher price. These requirements direct special attention to the study of explosives that can be produced from cheap and handy raw materials. Among such include all of the carbohydrates (cellulose, starch, and sugar, as well as the products which can be cheaply made from them) and the by-products of all large-scale organic chemical manufacturing processes as wood distillation, the manufacture of coke, the refining of petroleum, the paper industry (pulp liquor), the manufacture of soap, and the like. Biosynthetic processes for the fermentation of carbohydrates, such as that by which glycerine has been produced, have important relations to the explosives industry and, in general, the consideration of sources of raw materials is a large and important field.

The chief source of the cyclic compounds used for explosive production in the past has been the coal tar produced in the manufacture of coke. One ton of coal on distillation yields about 120 pounds of tar. From this tar, by distillation, about 6 pounds of naphthalene, 2.4 pounds of phenol and creosols, 1.9 pounds of benzene, 1.5 pounds of anthracene, 0.3 pound of toluene, and about ½ ounce of xylene can be gotten. As the United States annually produces in excess of 150,000,000 tons of coke (not all, however, by by-product distillation), here is a large potential source, which could be further increased by the general use of the Bergius, Fischer-Tropf, and other processes for the hydrogenation of coal. Cyclic hydrocarbons and other starting materials are also produced from petroleum in some of the cracking processes. It has recently been estimated that if necessary, by the use of the newer processes, the American oil industry could produce organic raw material, based on 1940 production figures, for 16.5 million tons of picric acid, 13.5 million tons of T.N.T., and 12.5 million tons of trinitroxylene by the use of 20% of the year's supply of gasoline. But on the other hand, there are some explosive compounds which would be more useful if their raw materials were more easily available—pentaerythrite tetranitrate, for example.

Other Chemical Methods of Nitration. In addition to the usual process, nitrogen groups can be introduced into organic molecules in a variety of ways, and for special chemical purposes the following listed methods often have advantages.

(1) $RX + AgNO_2 \rightleftharpoons RNO_2 + AgX$. This reaction yields a nitro compound principally only when R is CH_3.

(2) $RCH{=}CHR + 2\ NO_2 \rightleftharpoons RCH(NO_2)CH(NO_2)R$.

(3) $RC{\equiv}C{\cdot}R + 2\ NO_2 \rightleftharpoons RC(NO_2){=}C(NO_2)R$.

(4) N_2O_3 will nitrate many unsaturated compounds, usually by a series of reactions.

(5) $RX + HNO_3 \rightleftharpoons RNO_2 + XOH$, that is, the exchange of some other group for the nitro group. Many indirect nitrations are conducted by first introducing the sulphonate group and then replacing it, using either nitric acid, or a nitrate or nitrite salt.

(6) $RCHClCO{\cdot}OK + KNO_2 + H_2O \rightleftharpoons RCH_2NO_2 + KHCO_3 + KCl$.

(7) Other nitrating agents, such as metallic nitrates, metallic nitrites, methyl nitrate, ethyl nitrate, nitromethane, tetranitromethane, and nitroethane may be used and in some cases other syntheses are simultaneously accomplished, for example:

$$C_6H_5CHO + CH_3NO_2 \overset{ZnCl_2}{\rightleftharpoons} C_6H_5CH{:}CHNO_2 + H_2O.$$

(8) $RX + MNO_3 \rightleftharpoons RNO_3 + MX$.

(9) When nitric acid is used as the nitrating agent, many dehydrating agents may be employed other than sulphuric acid, for example, acetic anhydride, P_2O_5 and phosphoric acids, $ZnCl_2$, $AlCl_3$, and the like.

(10) Other solvents, such as chloroform, carbon tetrachloride, and benzene may be used with nitric acid, although they usually require a dehydrating agent also.

Stereochemistry of the Nitro Compounds. The special chemical methods of nitration have many advantages in individual cases—they may direct the place into which the incoming nitrogen is to go, they make certain reactions more efficient, and they may enable one to synthesize compounds otherwise not easily made. There are interesting laboratory problems, for example, in the production of α- or β-mononitroglycerine, or the symmetrical or unsymmetrical dinitrate, but commercially to date most of these methods are of little value.

The nitrates in general have the properties of esters, and nitroglycerine, which has already been described, may be taken as being to a degree typical of all. Since the nitrate group replaces the OH, there is little of the orientation problem here, except when all of the hydroxyl groups are not replaced; and since the explosive property increases with the number of nitrate groups introduced, the degree of nitration represented by nitrogen content in these cases is more important practically than the question of where the nitrate groups go.

In the usual nitration of cyclic compounds, however, there is always a number of possible points of attack, and the question of orientation here becomes important because, although the same fact holds, namely that explosive properties increase with the number of nitro groups, it is usually desired to produce a specific compound.

TABLE 26

ORIENTATION OF ENTERING NO_2 GROUP

FOR BENZENE

ortho-para	meta
Halogens	$—NO_2$ and $—NO$
—R where R is $—CH_3$, —C—C—R, or C_6H_5	$—HC{=}CH—R$
—OH or O—R	—CO—R and COOH
$—NH_2$ or $N{<}^{R}_{R}$	—CHO
—SH and S—R	$—SO_3H$ and $—SO_2$
but also some exceptions as —N=N—, and some —CH=CH—R	—CN
	but also some exceptions as indicated, and $—CCl_3$

Where the nitration is that of a cyclic hydrocarbon, the first nitro group enters a sensitive position—for benzene all positions are equivalent; for naphthalene the alpha position; for phenanthrene and anthracene, nitration results first in oxidation to the quinone on the central carbons followed by nitration in an alpha position on one of the unoxidized nuclei. On more complicated hydrocarbons, it usually follows these general principles.

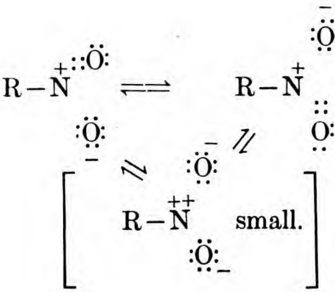
For additional groups on the benzene nucleus, the Rule of Crum-Brown and Gibson, to which others have added, maintains. If the group already present in the nucleus is attached by an atom which has some other atom joined to it by a multiple bond, the next entering group orients to a meta position; if the bonds are single bonds, the entering group orients to the ortho and para positions. Or in terms of electronic structure positive groups in the molecule orient ortho and para, and negative meta. For other cyclic systems other factors become more important with increasing complexity.

In general, however, all of the possible isomers are formed but in varying proportions, the indicated ones predominating.

The presence of other groups also influences the ease of nitration. With ortho or para orienting groups present, a low nitration temperature will increase the proportion of the para compound. The presence of methyl groups and in general the ortho or para orienting groups make nitration easier, and that of NO_2 and the meta groups, more difficult. Different groups have relatively different effects and in the order of decreasing ease we have approximately —OH, NH_2, CH_3, Cl, H, NO_2, SO_3H, COOH. Thus toluene is more readily nitrated than benzene, aniline and phenol still more easily, xylene more readily than toluene, and nitrobenzene with more difficulty than any of them. For the introduction of a third substituent, the effect of those already present is additive, but the effects may re-enforce each other, as in paranitrotoluene where both groups direct to the position that is ortho to the methyl group; or the effects may oppose, as in metanitrotoluene. It becomes increasingly difficult to introduce successive nitro groups, even in the case of toluene, where the methyl group is an aid. When introduced, the groups tend in successive steps to take the positions 1, 3, 5, although small amounts of meta compounds are formed. Trinitrobenzene is exceedingly difficult to make.

In the case of the polycyclic compounds, on nitration, the second nitro group tends to take the position analagous to the first if there is one, naphthalene yielding for example α-, α'-dinitronaphthalene; diphenyl, diothonitrobenzene. Succeeding groups follow the rules given in a general way, but for complicated compounds, the number of isomers formed rapidly becomes large, and the preparation of pure compounds by direct nitration is in practice almost impossible.

From the standpoint of electronic structure, nitro compounds have fairly large dipole moments, and are good ionizing solvents. Practically, the polynitro compounds are solvents and gelatinizing agents for nitrocellulose. The structure of the nitro group is represented by the following resonance equilibrium:



From the standpoint of the relation of chemical structure to explosive properties, nitro compounds throw no special light on the subject. Explosiveness and sensitivity increase with the number of NO_2 or NO_3 groups. Thus, while highly endothermic compounds like C_2H_2 are explosive and sensitive, nitroglycerine, which is an exothermic compound, is more sensitive and more powerful than most. This sensitivity is probably chiefly attributable, however, to the inherent instability of all nitrogen compounds by reason of the chemical inertness of nitrogen, and to the simultaneous introduction of more oxygen into the molecule with the NO_2 or NO_3 groups.

Mixed Acid. The first practical problem of nitration is the preparation of mixed acid, by weighing out and mixing sulphuric acid and nitric acid of the purity and concentrations suitable for the strength desired. Industrially, mixed acid is made on a large scale in large tanks or vats which must be corrosion resistant, and may be of steel, stoneware, or vitreous material. Mixing may be by mechanical paddles or compressed air. The tanks are usually and preferably arranged at a level to allow the acid to flow by gravity to the nitrator.

There is a temperature rise on mixing which may amount to from 20° to 30°C., and this waste heat may be utilized, or it may be necessary to wait for cooling or to provide cooling for low-temperature nitrations. A further temperature rise may occur on the addition of the substance to be nitrated; this rise may be so high as to make it necessary to nitrate by adding the substance first to the sulphuric acid, and then to add the nitric acid later as in the cases of picric acid from phenol or of tetryl from dimethyl aniline. The same method has been used for nitroglycerine.

The acid must be of suitable purity. This is usually controlled by analysis and rejection of the original acids which will be described in later chapters. Special requirements for individual nitrations have been mentioned; for example, suspended solids often cause difficulty in separation. Mixed acid, whether fresh or spent, is usually analyzed for total acidity by titration with $N/2$ KOH and nitrogen by the Du Pont nitrometer, from which its composition may be calculated on the assumption that the remainder is water. Free oxides of nitrogen may be determined by the formation of a purple color with a reagent of a few crystals diphenylamine dissolved in concentrated sulphuric acid (see page 46).

Nitration. From the mixed-acid tank the acid runs to the nitrators. These have many commercial forms and some of them have already been described. In the nitration process the following factors, which are interrelated, are of importance:

(1) Concentration of acid.
(2) Ratio of acid to raw material by weight.
(3) Temperature of nitration.
(4) Time of nitration.
(5) Ease of separation of the product.
(6) Purification of the product from traces of acid.
(7) Recovery of the spent acid.

Concentration and Acid Ratio. The concentration of mixed acid must first of all be suitable to conduct the reaction in question. This requirement usually means a high HNO_3 content and a low water content, and the tendency is toward mixed acid which contains practically no water originally because it is made from fuming sulphuric acid. However, the maximum nitration of cellulose is not obtained with completely nonaqueous acid, and where additional nitro groups have to be introduced, the tendency in practice as opposed to laboratory procedure is to carry the action out in successive steps rather than to use the extremes of concentration and acid ratio as well as extremes of other factors which might be necessary for nitration in one step. The related economies in materials used and the ease of acid recovery more than counterbalance the additional effort.

TABLE 27

FACTORS OF NITRATION

Process	Composition of acid			Temperature, °C	Time, minutes	Acid: substance ratio
	H_2SO_4	HNO_3	H_2O			
Nitroglycerine from glycerine	60	35	5	<30	20	8:1
Nitrocellulose from cotton	63	21	16	30	24	35:1 to 50:1
T.N.T. from toluene						
1st stage	76	23		55	30	7:1
2nd stage	76	23		83	60	7:1
3rd stage	about same, but different mixing			104	210	7:1
Picric acid from phenol	93% sulphonated first for 6 hours, at 95°C. + 70% HNO_3 <110°C.					
Tetryl from dimethylaniline	96% sulphonation, + HNO_3 or mixed acid at 70°C.					

Table 27 gives a summary of the commercial factors of nitration for a few materials. Taking the production of nitroglycerine or T.N.T. as typical:

$$\underset{92}{C_3H_5(OH)_3} + \underset{189}{3\ HNO_3} \rightleftharpoons \underset{227}{C_3H_5(NO_3)_3} + \underset{54}{3\ H_2O}$$

$$\underset{92}{C_7H_8} + \underset{189}{3\ HNO_3} \rightleftharpoons \underset{227}{C_7H_5(NO_2)_3} + \underset{54}{3\ H_2O}$$

Theoretically it requires about twice as much nitric acid by weight as organic material to make the explosive, and about 0.84 pound of nitric acid for every pound of explosive produced. The reactions are reversible and in practice a much higher ratio must actually be employed. Much of the excess acid can be and is recovered. H_2SO_4 used as a dehydrating agent functions also as a diluent. A 30% nitric acid concentration in the mix will nitrate almost anything satisfactorily, but when the nitration is difficult the nitric acid concentration may have to be raised to 50%.

As the nitration proceeds, it removes HNO_3 from the mixed acid and adds water to it. This is the condition which principally determines the lower limit for the ratio of acid to raw material, since the mixed acid not only must have the concentration necessary to conduct the reaction at the start, but also for efficient conversion of raw material into explosive the acid must retain at the end of the reaction a sufficient excess of HNO_3 and enough H_2SO_4 for proper dehydrating. For sulphuric acid this requirement in general means a final concentration of not more than 20% water and preferably less. Too great a difference in concentration of mixed and spent acid may be avoided in two ways: (1) by increasing the amount of acid in the ratio of acid to raw material, and (2) by increasing the concentration of HNO_3 in the mix, in which case, to some degree, 1 can be reduced. If the second method can be used it requires the handling of smaller total volumes and permits a smaller use of acids; and even though the excess is recovered, this is an economy.

In practice the ratio of mixed acid to raw material may vary from 5:1 to 50:1. For the reactions we are considering it is 8:1 for nitroglycerine, and about 20:1 for T.N.T. (remember that T.N.T. is a three-step process). A special property of the raw material may, however, fix the ratio, as we have seen in the case of nitrocellulose where the light, bulky, absorbent nature of the cotton requires at least 35:1 for proper coverage. In general, such considerations require a use of sulphuric acid, which may be recovered, to the amount of 2 to 3 pounds for every pound of explosive produced.

Example: Assuming nitroglycerine to be nitrated with 8 parts of a mixed acid containing H_2SO_4, 60%; HNO_3, 35%; and H_2O, 5% by weight, compute the concentration of the spent acid.

If we carry out the equation as written, we shall use 92 parts of nitroglycerine and 736 parts of acid. The following quantitative facts will then be true in theory:

	H_2SO_4	HNO_3	H_2O
Composition in parts of starting acid.......	441.6	257.6	36.8
Used or produced in parts................	—	189.0	54.0
Composition in parts of spent acid.........	441.6	68.6	90.8

Therefore, in the spent acid,

$$\%H_2SO_4 = \frac{441.6}{441.6 + 68.6 + 90.8} \times 100 = \frac{44{,}160}{600} = 73.2\%$$

$$\%HNO_3 = \frac{68.6}{600} \times 100 = 11.4\%$$

$$\%H_2O = \frac{90.8}{600} \times 100 = 15.1\%$$

While actual concentrations of spent acid are usually determined analytically by the methods used for any mixed acids, this calculation is frequently useful since the calculated percentage is usually close enough to the truth to be a satisfactory answer to many questions.

In actual practice the concentration and acid ratio may be influenced by a number of other factors, such as ease of separation of the product, ease of recovery of the spent acid, and, where direct separation is employed (as is usual today), solubility of the product in the spent acid which may reduce the yield.

Mixed acid is made up from the commercial grades of nitric acid and sulphuric acid which are available. For nitric acid, the usual commercial highly concentrated variety is of 93% concentration and of specific gravity 1.489. Sulphuric acid has the various fuming grades; monohydrate is of 100% concentration, and commercial concentrated sulphuric acid is about 95% concentrated, with a specific gravity of 1.834. It is obvious that the only mixed acid shown in Table 27 which could be made up from the commercial concentrated grade, is that required for nitrocellulose: H_2SO_4, 63%; HNO_3, 21%; and H_2O, 16%. For a completely nonaqueous mixed acid, fuming sulphuric acid must be used, but practically all mixed acids can be made from commercial highly concentrated nitric acid, 20% fuming sulphuric acid which is liquid and easy to handle, and some water if necessary, and these are usual starting materials.

EXAMPLE: How would you make up a mixed acid suitable for nitrocellulose nitration from the commercial highly concentrated acids?

	H_2SO_4	HNO_3	H_2O
1,000 grams of mixed acid contains, grams........	630	210	160
Commercial acid contains, grams per cubic centimeter (specific gravity × % concentration).....	1.742		0.0917
Commercial acid contains, grams per cubic centimeter (specific gravity × % concentration).....		1.385	0.1032

You would, therefore, require $\frac{630}{1.742} = 361.7$ cc. of concentrated sulphuric acid or 663.3 grams; and $\frac{210}{1.385} = 151.6$ cc. or 225.8 grams of concentrated nitric acid. But from these volumes or weights we should also have introduced 33.2 grams of water from the sulphuric acid and 15.8 grams from the nitric acid. We therefore require $160 - (33.2 + 15.8) = 111$ grams or cubic centimeters more water. Hence, the required acid could then be made by mixing:

	Weight, parts	Volume, parts
Water	111	111
Concentrated H_2SO_4	663.3	361.7
Concentrated HNO_3	225.8	151.6

Temperature of Nitration. Temperature must be carefully watched during nitration, as fortuitous circumstances may cause variations which become dangerous. In general, a rise in temperature of 10°C. at least doubles the speed of chemical reaction. Since the ease of nitration varies from substance to substance, the temperature factor is one which in theory can be of valuable assistance with difficult nitrations. In practice, however, mixed acid is a powerful dehydrating agent due to one component, and a powerful oxidizing agent due to both. There is always, therefore, the possibility of side reactions of these natures with the raw material; they always occur to some extent. These reactions reduce the yields. Moreover, since they are in general highly exothermic, they may result in decomposition which, if uncontrolled, may become explosive. High temperatures in nitration are therefore both inefficient and dangerous. Nitration is usually carried out at ordinary temperatures or below them, and it is important to provide cooling. The usual method of cooling is by the use of water coils in the nitrator, together with good stirring by compressed air or paddles. The temperature of 100°C. used in the third step of the T.N.T. process is exceptional. The water used, however, is usually not artificially cooled, and so in large plants degree of cooling and over-all efficiency may vary in summer and winter.

The side reactions in some cases, as picric acid from phenol, tetryl from dimethylaniline, and some other similar compounds, prevent direct nitration by mixed acid, and require the solution of the raw material in the sulphuric acid, and the slow addition of nitric acid or mixed acid to that solution. In the Boutmy-Faucher process for nitroglycerine, the glycerine is first dissolved in sulphuric acid, since this step has a high heat of reaction, and this mixture is cooled and poured into the mixed acid.

Time of Nitration and Separation. The time of nitrations in general is a function of the specific reaction, but for most important commercial nitrations, with the proper acid, nitration takes place fairly rapidly, the entire cycle of operations being often completed in 35 minutes. The third step in the toluene nitration is exceptional, and some other excellent explosives such as trinitrobenzene have not become as important as they might be because of the unusual difficulty of nitration.

Since the nitration reaction is reversible, it is important to remove the product from contact with the mixed acid as rapidly as possible, at the point of maximum nitration desired. In the early days of explosive production this was done by "drowning the charge," that is by dropping it suddenly into a large volume of water, from 5 to 10 times its own volume. This method of separation is still an excellent one, and as a rule will give a maximum yield of product, since the product is usually soluble to some extent in the relatively strong spent acid and the degree of solubility is sometimes appreciable. A disadvantage is, however, that acid recovery from the spent acid, which in earlier days of smaller production was often discarded, becomes unduly expensive. The use of the drowning method is now largely limited to emergency safety procedure; on a sudden hazardous temperature rise during nitration, the charge may be dropped by means of dump valves into large drowning tanks situated directly beneath the nitrators. Where the product is completely soluble in any spent acid which would result from any workable starting mixed acid, drowning must still be used. A subsidiary determinant for the concentration of the original mixed acid is then that it yield a spent acid in which the solubility of the product is as near minimal as possible.

Where the nitration product is a solid, it is usually separated from the spent acid by centrifuging. Where the product is, at any workable temperature, a liquid largely insoluble in the spent acid, it is usually allowed to stand and separate out due to its difference in specific gravity. This process may take place either in the nitrator or in a separator distinct from it. In any event, such separation will not be completely sharp, since it must be fairly rapid or the yield will be reduced. After the quick separation the spent acid must be allowed an afterseparation in which small quantities of the product will be saved. The afterseparation will either increase the yield or, unless the small residual quantities of explosive are removed, further treatment of the spent acid may be hazardous. This danger places still another criterion on the mixed-acid concentration, in that the starting mixture must yield a spent acid of sufficient difference in specific gravity from the product to permit a reasonably rapid, as well as efficient separation.

Experiment. *A Study of the Nitroglycerine Reaction.* (**Caution!** *Remember you are working with nitroglycerine here!*) 100 grams of 93% nitric acid are weighed into an Erlenmeyer flask, and 10 grams of glycerine, weighed by difference, is put into the same flask. Considerable heat is developed, and the flask is immediately placed in ice water, mildly stirred by shaking, and allowed to stand in ice water for 1 hour. During the hour, at 5-minute intervals, remove by pipette 1 cc. of the acid, and put each such sample into 50 cc. of water in separate Erlenmeyer flasks. These, along with a 1-cc. sample of the original acid, should be titrated as rapidly as possible with standard base. Plot the concentration of acid against time.

At the end of the hour, pour the remainder of the mixture into 300 cc. of ice water, and separate and wash the oil with minimal portions of water. Weigh the oil. Make an allowance for a solubility of nitroglycerine in the final acid of 10 grams per liter. From your observations, compute the equilibrium constant for the nitration of glycerine, assuming equilibrium to be reached at the end of the hour. Was it so reached? The use of sulphuric acid increases both the yield and the rate of nitration.

Purification from Traces of Acid. The purification of the product of nitration from the spent acid is an important and at times a difficult problem. The minimum first step is always thorough washing with water, using 5 to 10 times the quantity of product each time, and repeating several times. In order to stabilize nitrocellulose, prolonged boiling with water (up to 100 hours) is necessary. In all cases, the removal of the last traces of acid is difficult, and may usually be done by the use of 2% to 3% Na_2CO_3 solution at temperatures sometimes up to boiling, without too great hydrolysis. This must be followed by further washing with water, for the product must be neutral and contain neither base nor acid.

Traces of acid will form in the product on storage after the most careful purification, and may cause accelerated decomposition. A material may be incorporated in the finished product to absorb these materials, as diphenylamine is put in smokeless powders, and thus improve keeping qualities.

Recovery of Spent Acid. As we have seen, in general, about 0.84 pound of nitric acid and no sulphuric acid are consumed theoretically in the production of 1 pound of explosive. Practically, with wide variation, about 1.5 pounds of HNO_3 and about 3 pounds of H_2SO_4 are used, and most of the difference remains in the spent acid. In the early days, little effort was made to recover this material, but today such an attitude would be economically fatal at once.

There are two general types of methods: (1) fortification and (2) denitration. These two are really complementary, rather than alternative methods, although (1) may not in every case be possible.

Fortification involves the addition to the spent acid of the proper amount of a stronger mixed acid required to bring it back to the nitrating composition. It may also be necessary to add fuming sulphuric acid to take care of some of the water. The strongest mixed acid which can be made from 20% fuming sulphuric acid and ordinary commercial highly concentrated nitric acid, which are usually employed, is about 41% HNO_3 and 59% H_2SO_4, and this is a familiar strength of fortifying acid. Thus, as we have seen, using a mixed acid of the ratio $H_2SO_4:HNO_3:H_2O$ of 60:35:5, the spent acid has a theoretical composition, which is practically about true, of 73:12:15, to use round numbers. Now observe:

	H_2SO_4	HNO_3	H_2O
300 grams of nitrating acid contain (grams).......	180	105	15
100 grams of spent acid contain (grams)..........	73	12	15
Hence, there is a deficiency of (grams)...........	107	93	

The deficiency has to be made up with fortifying acid. It could be done obviously with 200 grams of a fortifying acid of a composition $H_2SO_4:HNO_3 = 53:47$. This acid strength is not easily attainable and would not be used. Further, fortification here would result in an increase in volume of nitrating acid of more than 100%.

This problem places an additional criterion on the strength of the original mixed acid which it is not always possible or desirable to meet. Where it is possible, the concentration of nitrating acid should be chosen to yield a spent acid which may be readily fortified by a conveniently prepared fortifying acid, without too large a volume increase. Where it is not possible, fortification is not employed. However, fortification is frequently useful in multistage nitration processes, where the spent acid from one of the later stages may be fortified to be suitable for one of the earlier steps, as in the case of T.N.T. Fortification involves no particular manufacturing problem, but merely the preparation of more than one kind of mixed acid by the usual procedure.

Even if fortification be employed, there is an ultimate limit to its use in terms of the accumulation of impurities and the increase in volume. In any circumstance, the final problem of spent-acid recovery resolves itself into the separation of the spent acid into its component acids with accompanying purification. This process is termed denitration.

A denitration unit consists essentially of a denitrating tower, air condensers, and absorption tower, the flow of material is in that order. The denitrating tower is a cylindrical one with acid-resistant lining and more or less filled with acid resistant material (see Chapter 9), designed to break up the stream of spent acid which flows down from the top of the tower. The acid meets a stream of hot gas coming up the tower, which removes from it practically all of the nitric acid and oxides of nitrogen and carries them on through the air condensers, and at the same time oxidizes fairly completely all of the organic impurities which the acid contained. If steam is used for heating, the sulphuric acid obtained at the bottom of the tower may be diluted; if hot gases, it may be concentrated; but in practice both changes are usually small. A relatively small tower 25 feet in height and 3 feet in internal diameter may denitrate as much as 100 tons of acid in 24 hours. A typical strength is 78% (60°B.), and the acid will be fairly pure and colorless.

The nitric acid vapors pass through the air condensers, where air is first injected to convert the oxides of nitrogen as far as possible to

NO_2. The nitric acid condenses in the air condensers to form a fairly strong nitric acid of about 63% (40°B.), and the oxides of nitrogen pass on to the bottom of the absorption tower (see Chapter 10) which are usually arranged in pairs to permit a recirculation of the gases, where they rise against a water stream to be converted into nitric acid.

$$3\,NO_2 + H_2O \rightleftharpoons 2\,HNO_3 + \uparrow NO$$

This nitric acid is usually a little weaker than the first obtained, but operating conditions can be adjusted to produce the same strength.

The acids thus obtained are a little weaker than those ordinarily used in most explosives operations, but they can be used for some purposes, particularly the nitric acid. They are, however, usually disposed of for other chemical purposes. Many uses have been proposed for spent acids to replace denitration, and spent acid from one process might be directly suitable for another.

The denitration process may be dangerous if there has been an insufficient removal of the product of nitration from the spent acid. This is particularly true in the case of nitroglycerine manufacture.

Discussion Questions and Exercises

1. Review the topics of chemical equilibrium and reversible reactions.

2. Read the article "Progress in Petroleum," Dr. Gustav Egloff, *Science*, 91, 533 (1940).

3. Amplify the synthetic reactions on p. 140 more completely.

4. Prepare tables, from a chemical handbook and elsewhere, of the known nitro derivatives of benzene, toluene, xylene, naphthalene, phenanthrene, anthracene, chrysene, and the like. Make some of the explosive calculations for them.

5. Read the article "Non-Aqueous Solutions," Charles A. Kraus, *Science*, 90, 281 (1939).

6. Practice the solution of numerical problems involving the preparation of large batches of mixed acid.

7. What is the Nernst approximation equation? (See p. 172.)

8. Review the manufacture of nitrocellulose as you read the steps of the nitration problem.

9. Calculate the composition of the spent acid in the various nitration processes described herein.

10. What other uses of spent acid can you think of?

11. Attempt to formulate a procedure for the nitration of some substance with which you are not familiar, and then compare your conclusions with a procedure which has been used.

CHAPTER 9

Sulphuric Acid

Importance. Sulphuric acid is probably the most important single chemical substance which is manufactured industrially. It has been said that the degree of civilization of a country may be estimated by its annual output of the acid. The point of this remark is that modern civilization is largely dependent upon the extent of manufacturing development, and, since sulphuric acid enters directly or indirectly into almost all large-scale manufacturing operations, no country could be very largely industrialized without having a considerable output. Table 28 shows the world production of sulphuric acid in 1927.

TABLE 28

WORLD PRODUCTION OF SULPHURIC ACID (1927)

Country	1,000 Metric Tons of 62.5% H_2SO_4
United States	6,300
France	1,840
Germany	1,800
Great Britain	1,300
Italy	1,075
Belgium	740
Poland	320
Spain	230
Denmark	175
Holland	150
Sweden	140
Serbia	100
Hungary	80
Austria	70
Switzerland	50
Total	14,580

Statistics of sulphuric acid production, like those of the steel industry, are commonly employed as barometers of general business conditions. While the present potential capacity for production is probably much greater than these figures indicate, possibly more than twice as high, especially for Germany, and Japan undoubtedly now has large volume production, these figures are higher than the production of later depression years and have only been reached again since the war began. One of the most interesting of industrial phenomena is the way in which the United States has outstripped Germany in this field since the First World War. German production as early as 1913 was 2,700,000 tons. Ours is now probably near 8 millions.

TABLE 29

PERCENTAGE USE OF TOTAL OUTPUT OF SULPHURIC ACID IN VARIOUS AMERICAN INDUSTRIES (1935)

Industry	% Use
Fertilizer	22.6
Petroleum refining	16.2
Chemicals	14.7
Steel pickling	10.4
Dyes and coal products	9.7
Metallurgy	8.4
Paints and pigments	4.5
Explosives	2.9
Textiles	1.5
All others	9.1

While sulphuric acid is important in the manufacture of explosives this is by no means its largest use. Table 29 shows the percentage use of the total output of sulphuric acid in various American industries in 1935. Explosives represented the second smallest use but the total quantity required was nevertheless in excess of 175,000 tons.[1]

History. Sulphuric acid has been known since the early Middle Ages, and was probably first prepared by the Arabian alchemists. Geber, in the *Sum of Perfection*, describes a method of preparing what was probably chiefly nitric acid (and also *aqua regia* by dissolving chloride in it) from copper sulphate, alum, and niter by distillation; but this reagent may have contained some sulphuric acid because of the method of preparation. Condensation of the fumes obtained by heating copperas or alumina may have been an early method. Distillation of ferrous sulphate with sand was another. Valentinus (*circa* 1450) is credited with preparing sulphuric acid by burning sulphur with potassium nitrate, the earliest prototype of one of the modern processes. Roebuck of Birmingham, England (1746), is said to have been the first to carry this reaction out in lead chambers. Ward, at Richmond-on-the-Thames in 1758, is said to have made the first successful commercial preparation, using this reaction with the mixture suspended in a large glass globe partially filled with water, which slightly later evolved into an apparatus not greatly different from that commonly used in lectures in general chemistry to illustrate the chamber process. The acid thus prepared is quite impure, containing sulphur dioxide and oxides of nitrogen, although it may be and was quite concentrated if so desired. Modern large-scale production is said to have begun with the manufacture from pyritic shales in Bohemia, and at Nordhausen in Germany. Sulphuric acid containing excess SO_3, "fuming sulphuric acid," is sometimes still referred to as Nordhausen acid.

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[1] Actually the figures are somewhat misleading, since in explosive manufacture the sulphuric acid is largely not destroyed but merely diluted. Present explosives practice is to recover the acid in several ways. The actual use of sulphuric acid in the explosive industry represents, therefore, several times this figure, which indicates only the amount withdrawn by the industry from the general market.

Chemical Considerations. Sulphuric acid has the formula H_2SO_4 and its anhydride is SO_3, which appears to exhibit dimorphic forms known as α and β, are usually assigned the formulas SO_3 and $(SO_3)_2$ respectively, and have slightly differing properties, as follows:

	Molecular weight	Crystal form	Specific gravity	Melting point °C.	Boiling point °C.
α	80.06	White triclinic	solid 2.75 liquid $1.925^{13°C.}$	16.8	44.8
β	160.12	silky fibrous needles	liquid 1.97	$32.2^{398mm.}$	44.6

The β modification sublimes at 50°C. and melts only under diminished pressure. The anhydride combines readily with water to form the acid; but on a large scale, gaseous SO_3 can be bubbled through water many times successively without dissolving because the gas bubbles acquire a fog of liquid sulphuric acid around their periphery which prevents good contact between the SO_3 and water. Steam and gaseous SO_3 condense together readily to form the acid, but practice is usually to dissolve the SO_3 in concentrated sulphuric acid to form fuming sulphuric acid, thus avoiding the formation of the fog; the fuming acid may then be diluted with water.

SO_3 is readily made by heating any of the heavy-metal sulphates, or by the dehydration of the acid with P_2O_5. Such methods are not economically suitable for the production of the acid. SO_2, on the other hand, is readily and cheaply made by burning sulphur or iron pyrites, FeS_2, and is obtained in the flue gases from the roasting of all sulphide ores. Many of the metallurgical industries, in particular copper, make sulphuric acid from this source. SO_2 is a gas, molecular weight 64.06, melting point $-72.7°C.$, boiling point $-10.0°C.$, specific gravity liquid $1.434^{0°C.}$, solubility 22.8 grams per 100 cc. of water at 0°C., the solution being acidic and containing H_2SO_3. SO_2 combines with oxygen to form SO_3.

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 + 45{,}200 \text{ calories.}$$

The reaction is exceedingly slow at ordinary temperatures, is reversible, and obviously at higher temperatures the equilibrium tends to favor the decomposition more and more. At 400°C., SO_3 is about 1% dissociated; at 700°C., 40%; and above 900°C., dissociation is practically complete. By itself, the reaction is useless as a means of preparing SO_3. Many things, however, will catalyze the reaction at temperatures which yield, under proper conditions, nearly complete conversion: Cl_2, various oxides of nitrogen, platinum, $Fe_2O_3 + CuO$, V_2O_5, silica gel, and others. In recent years much research has been done on the catalysts for this reaction. Thus the action of V_2O_5 as a catalyst is promoted by the presence of iron and potassium oxides; platinum may be used as foil or as wire mesh, or it may be carried on silica gel, asbestos fiber, or on the surface of calcined magnesium sulphate (Grillo process). Platinum and vanadium oxide function effectively in the neighborhood of 400°C. and therefore can in theory give nearly 100% yield, whereas Fe_2O_3 exhibits its maximum efficiency around 550°C. where the theoretical yield of SO_3 is only about 70%. Platinum as a catalyst is remarkably sensitive to poisoning and very minute quantities of impurities, particularly arsenic and halogen, render it quite inactive. The other catalysts are not so sensitive, and oxides of nitrogen are very insensitive. The two principal commercial processes for making sulphuric acid are based on these catalysts: the chamber process which initially and still largely uses oxides of nitrogen; and the contact process, which initially and still largely uses platinum, although now in several forms, and also after the use of other catalysts—or it may use other catalysts only.

The Chamber Process. This process is the oldest large-scale method of making sulphuric acid. Despite severe competition by the contact process, it still survives as the important method of producing at least certain grades of the product. A summary of the principal steps and apparatus is shown in the flow sheet, Figure 19.

A. Raw materials. In early days, sulphur dioxide was produced in furnaces, or sulphur stoves, from iron pyrites:

$$4\ FeS_2 + 11\ O_2 \rightleftharpoons 2\ Fe_2O_3 + 8\ SO_2.$$

Later in England and also in the United States, the roasting of copper pyrites for the production of copper become a large and cheap source of raw material, and of course any by-product gas containing SO_2 may be employed as a starting point. More recently, with the tremendous development of the Frasch process, pure sulphur (which is burned in the sulphur burners) has become the principal source. This material yields the purest gas, for pyrite gas always contains such impurities as arsenic, lead, selenium, fluorine, carbon dioxide, organic material, and ammonia. Such impurities must be carefully removed in contact processes because of poisoning effects, and some of them are objectionable even in the chamber process because they tend to cause loss of oxides of nitrogen by reaction. The burner gas should contain from 7% to 8% of SO_2 by volume and some excess of oxygen, say 9% to 9.5% total. In burning pure sulphur, 10% to 11% SO_2, with this condition, is readily obtained.

Where pure sulphur is not used, some purification of the gas may be necessary after burning, at least to the extent of dust collecting chambers at this point, but in designing plants every effort is made to avoid heat losses as far as possible between the burner and the next step.

B. The Glover Tower. The Glover tower is a large cylindrical structure consisting of a lead shell lined with vitrified brick and containing a similar brick checkerwork, or flints, supported on semicircular arches. At the top of the tower are two lead-lined cisterns. Into the top of the tower are fed two varieties of acid: H_2SO_4 from the chambers at 60% to 70% strength, and sulphuric acid containing oxides

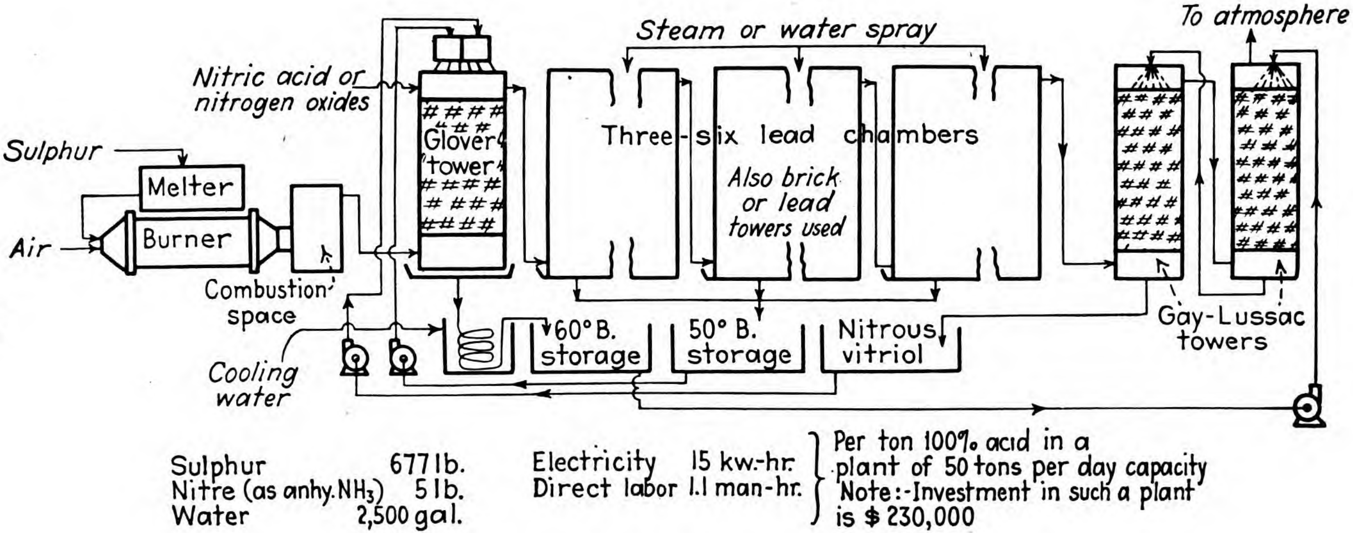

FIGURE 19: **Sulphuric Acid (Chamber Process)**
(Courtesy of *Chemical and Metallurgical Engineering*)

of nitrogen—largely nitrosyl sulphuric acid, $H(NO)SO_4$—from the Gay-Lussac towers. Below the cisterns, nitric acid vapors or oxides of nitrogen are introduced. The falling stream of liquid meets the rising stream of gas from the burners, the checkerwork aiding good mixing, and a variety of things happen:

(1) Sulphuric acid is synthesized by the chamber reactions, in the liquid phase.

(2) The nitrosyl sulphuric acid is converted into H_2SO_4 and the liberated oxides of nitrogen are swept onward into the chambers.

(3) The heat of the rising burner gases effects a considerable concentration of the sulphuric acid by the time it reaches the bottom of the tower, the water removed being carried upward as steam.

The net result is that about 50% of the acid yield of the plant is obtained from the Glover tower, and this is the strongest acid, of strength about 80%. It is cooled by water-jacketed lead lined coolers, and part of it is run to the top of the Gay-Lussac tower to be used in the recovery of oxides of nitrogen.

C. The Lead Chambers. The gases swept out of the Glover tower are passed into the lead-lined chambers that give the name to the process. These chambers are merely large lead-lined rooms through which the gases drift, are mixed, and react, forming liquid sulphuric acid which condenses on the floor.

The chambers are very large in area and the space they require is one of the costly aspects of the process under some conditions. They may be 150 feet by 30 feet by 30 feet, or greater in size, and have capacities in excess of 200,000 cubic feet. They may be elevated above the ground to give some hydrostatic head so that the acid does not have to be pumped, and consist of a framework of timber or steel lined with lead sheets. These sheets are carefully welded together. Lead is used because it is the cheapest material that will withstand the corrosion to which it is subjected, and it must be of the highest purity or it will corrode rapidly. Even so, lead reacts to form $PbSO_4$. At about 60% strength of H_2SO_4, the $PbSO_4$, however, forms a firmly adherent coating and the rate of corrosion is slow. Above this strength, the acid tends to dissolve the coating and below it the coating is not firmly adherent. Either condition causes more frequent shutdown for repair, and so conditions in the chambers must be fairly closely controlled. Chamber-process acid always contains lead, unless it has been further purified.

Mixing is not complete in one chamber and practice is to use several in series, the successive ones being smaller. Any number might be used with theoretical increases in efficiency, but in practice six is about the maximum, and three is usual. A total yield of H_2SO_4 representing 98% of the sulphur content of the burner gases is usual. In one recent modification of this process, one small chamber is said to be equal in efficiency to all of the large ones. This chamber is equipped with a complicated system of baffles by which the gases are forced to follow a very circuitous path, and secures very good mixing and reaction.

The gases entering the chambers from the Glover tower contain SO_2, O_2, steam, and oxides of nitrogen (as well as residual nitrogen from the air and impurities from the source)—that is to say, all of the material necessary for reaction. In theory no addition is necessary but in practice, jets in the chamber introduce steam, air, and more oxides of nitrogen, that is, everything but SO_2. In modern practice the water is usually in the form of a finely atomized spray rather than as steam, and while it may be omitted from the first chamber because of water carried over from the Glover tower, it is usually introduced even there to control the concentration of acid formed.

Nitric acid vapor, rather than oxides of nitrogen, was formerly used, and was prepared by the usual process of distilling niter with sulphuric acid in cast iron retorts, "niter pots." The total amount of nitric acid required is about 3% of the weight that would be required on the assumption that the process was a straight oxidation of SO_2 to H_2SO_4 by nitric acid.

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

$$2\ H_2O + 3\ SO_2 + 2\ HNO_3 \rightleftharpoons 3\ H_2SO_4 + 2\ NO$$

In practice much of the nitric acid is recovered in the final step, but as the reaction is in part oxidation, any reduction of the nitrogen below NO (for example, to N_2O or N_2) represents a loss, as these materials will not function catalytically and are not recovered, where all of the other oxides will function and are recovered. In modern practice, nitric acid may not be used but oxides of nitrogen produced by the catalytic oxidation of ammonia by the Ostwald process (see page 184). Under any circumstances, a certain amount of loss always occurs and the presence of certain impurities in the burner gas—for example, NH_3 and organic materials—will increase cost very objectionably. A reasonable consumption of nitrogen is five pounds per ton of H_2SO_4. At the exit of the last chamber the residual gas should contain no SO_2, but only air and impurity residues, moisture, and oxides of nitrogen which must be recovered.

The acid which collects on the floor of the chambers is usually about 50°B. (= 63%), and is run to storage. Part of it may be by-passed to the top of the Gay-Lussac tower for the recovery of oxides of nitrogen at the start of a cycle of operation where there is no Glover tower acid available.

D. The Gay-Lussac Towers. The residual gases from the last chamber are run to the bottom of the Gay-Lussac towers. There may be one, two, or several of these. They are larger in size than the Glover tower, possibly 30 feet in diameter and 100 feet high. They are built of lead shells lined with acid-resisting brick and filled, space being left between the pieces of filling, with tiles, pieces of glass, coke, or earthenware rings; and sometimes pieces in alternate layers are arranged perpendicularly to each other. A stream of sulphuric acid, either from the Glover tower or by-passed from the chambers, trickles down, and meets the stream of rising gas from the last chamber. The acid then absorbs the oxides of nitrogen to form nitrosyl sulphuric acid, $H(NO)SO_4$, which is led to the top of the Glover tower. (Gas-liquid countercurrent processes in towers of similar design are generally useful in all chemical industries.) In practice there are usually at least two Gay-Lussac towers, with a draft-control fan between them which directs the flow of gas for the entire process. Under any circumstances, absorption of the oxides of nitrogen is not perfect, but this incomplete absorption represents part of the necessary loss, for at this point the flue gases leave the plant.

Chemistry of the Chamber Process. The nature and mechanism of the chemical reactions of the chamber process have been the subject of a great deal of research. The production of SO_2 is a straight and obvious oxidation of sulphur or sulphur-containing material, and any gas containing SO_2 may be used as a starting material although the compositions already indicated are the most efficient. Dispute centers about how SO_2 is converted into H_2SO_4. Nitric acid will oxidize SO_2 to H_2SO_4, but the actual amount needed is much less than stoichiometrical relations require, and NO and all of the higher oxides of nitrogen will function in the presence of oxygen. The essence of the reaction is the replacement of the relatively slow direct combination with oxygen by other more rapid chemical reactions, and the problem is to demonstrate those reactions.

Berzelius originally proposed NO_2 as a chemical catalyst and the mechanism:

$$SO_2 + NO_2 + H_2O \rightleftharpoons H_2SO_4 + NO,$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2,$$

and so on. After extensive study, Lunge proposed N_2O_3 and the mechanism:

$$2\ SO_2 + O_2 + H_2O + N_2O_3 \rightleftharpoons 2\ H(NO)SO_4 \qquad (1)$$

$$2\ H(NO)SO_4 + H_2O \rightleftharpoons 2\ H_2SO_4 + N_2O_3 \qquad (2)$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2$$

where the presence of N_2O_3 is accounted for by a preliminary oxidation, regardless of the starting material, as

$$SO_2 + 2\ NO_2 \rightleftharpoons SO_3 + N_2O_3$$

or

$$H_2O + 2\ SO_2 + 2\ HNO_3 \rightleftharpoons 2\ H_2SO_4 + N_2O_3.$$

Sulphuric acid may be made, and often is made as a lecture experiment, in the apparatus shown in Figure 20. The large bulb is first filled with oxides of nitrogen and also contains a little water vapor. Under these conditions, if SO_2 is slowly run in, the brown color of the oxides of nitrogen slowly disappears and white rosettes of solid crystals form on the walls of the vessel. These crystals are nitrosyl sulphuric acid. Then, if steam be run in, they disappear with a faint hissing noise, with the formation of H_2SO_4 and ultimate regeneration of the oxides of nitrogen. This behavior illustrates and confirms reactions (1) and (2). In a properly operating chamber-process plant these reactions take place successively and "chamber crystals," as they are called, are not normally formed, but may be formed if the amount of water introduced is too small. What actually happens, over all, in terms of this theory would be

$$2\,SO_2 + O_2 + H_2O + N_2O_3 \rightleftharpoons 2\,H_2SO_4 + N_2O_3.$$

It had been observed often that in the course of this experiment instead of white chamber crystals one may get a deep purple or violet product, and the corresponding coloration in the liquid acid. The violet material is very unstable, and not always formed. Berle[2] succeeded in isolating and identifying the "violet acid" as $H_2SO_4 \cdot NO$ or possibly $SO_5 \cdot NH_2$. Reasoning from this experiment, Berle re-

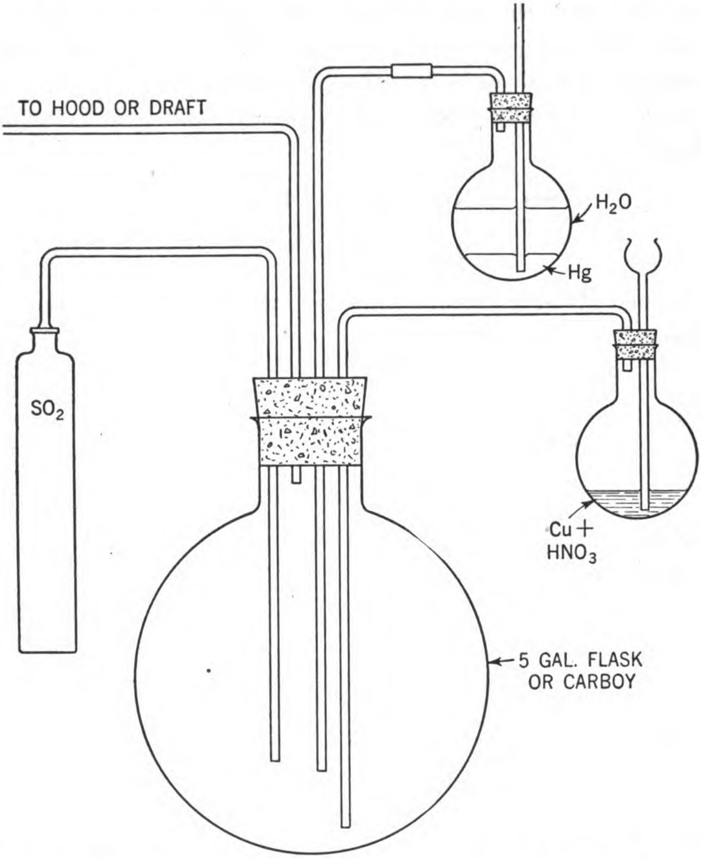

FIGURE 20: **Lecture Preparation of H_2SO_4 by the Chamber Process**

turned to NO_2 as the catalyst, and proposed the following mechanism, which may be accepted for the present:

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[2] Berle, *Trans. Am. Inst. Chem. Eng.*, 31, 193, 1935.

$$4\ SO_2 + 2\ H_2O + O_2 + 4\ NO_2 \rightleftharpoons 4\ H(NO)SO_4, \qquad (3)$$

$$2\ H(NO)SO_4 + 2\ H_2O + SO_2 \rightleftharpoons H_2SO_4 + 2\ H_2SO_4 \cdot NO, \qquad (4)$$

$$H_2SO_4 \cdot NO \rightleftharpoons H_2SO_4 + NO, \qquad (5)$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2, \qquad (6)$$

$$2\ H_2SO_4 \cdot NO + NO_2 \rightleftharpoons 2\ H(NO)SO_4 + NO + H_2O, \qquad (7)$$

and also the side reactions

$$H_2SO_3 + NO_2 \rightleftharpoons H_2SO_4 + NO \qquad (8)$$

and

$$H_2SO_3 + NO_2 \rightleftharpoons H_2SO_4 \cdot NO. \qquad (9)$$

In terms of this hypothesis the chemical reactions in the previously described process may be explained as follows:

A. In the lead chamber, reactions (3), (4), and (5) occur in rapid succession so that one has essentially, over all, the older Berzelius mechanism since regeneration of the NO_2 is accounted for by equation (6).

B. In the Glover tower, a complete synthesis is represented by equations (3), (4), and (5) in the liquid phase, as well as (4) and (5) separately, since $H(NO)SO_4$ is introduced at the top of the tower, and the additional water is furnished by the dilute acid. The burner gases contain enough excess oxygen to account for the appearance of the nitrogen as NO_2 in the chambers.

C. In the Gay-Lussac tower the absorption of the oxides of nitrogen of all degrees of oxidation from NO up, to form $H(NO)SO_4$,

$$H_2SO_4 + NO \rightleftharpoons H_2SO_4 \cdot NO, \qquad (\alpha)$$

$$2\ H_2SO_4 \cdot NO + NO_2 \rightleftharpoons 2\ H(NO)SO_4 + NO + H_2O,$$

$$H_2SO_4 + 2\ NO_2 \rightleftharpoons H(NO)SO_4 + HNO_3, \qquad (\beta)$$

$$2\ H_2SO_4 + N_2O_3 \rightleftharpoons 2\ H(NO)SO_4 + H_2O, \qquad (\gamma)$$

and so on.

It is interesting to note that one of Berle's conclusions is that to conduct the chamber process under pressures greater than atmospheric would result in higher efficiency and economy. This proposal has not been put in effect.

Chamber-process Acid. The acid produced by the chamber process contains lead as an impurity and runs from 60% for the chamber acid to 80% H_2SO_4 for the Glover-tower acid. These are about the maximum concentrations that can be achieved by heating the dilute acid in lead-lined pans using waste heat from the burners to economize fuel. To get higher concentrations in this process certain additional procedures may be used.

The Cascade System. A series of silica or silica-iron basins are arranged along an inclined heating unit through which are run waste gases or hot gases from a firing mechanism at the bottom (see Figure 21). Dilute acid flows into the top basin and overflows successively to the bottom, becoming more concentrated by the heating as it does so.

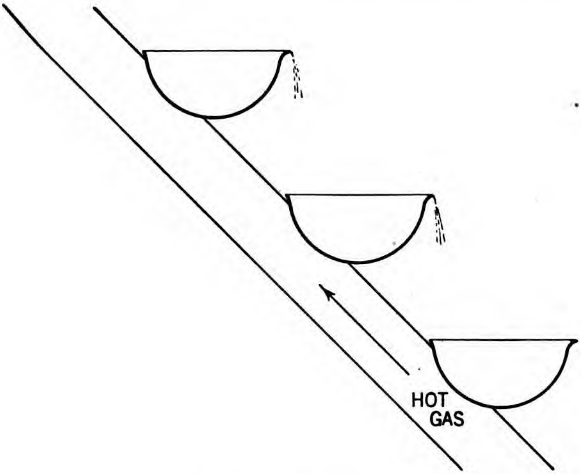

FIGURE 21: **Cascade System of Concentration**

The Gaillard Tower. This is a tower generally similar in construction to a Gay-Lussac tower. Hot furnace gas is introduced at the bottom and dilute acid is sprayed in at the top. The acid concentrates as it flows down, to about 93%.

If contact-process acid is available, acid of any desired strength may be made by mixing the two kinds.

The Contact Process. Contact processes for the production of sulphuric acid began to be developed in England by Squire and Messel during the last quarter of the nineteenth century, and simultaneously in Germany. Holmes[3] gives credit to Knietsch (Germany, 1901) for its first commercial success. Contact processes have evolved many kinds of plants, including among the better known types those that might be described as the American since they are used in the United States, the Badische, the Mannheim, the Tentelew, and the Grillo. All are more or less alike in general, and differ only in the nature of the catalysts used, and in the way in which subsidiary procedures are conducted. The essential steps are:

A. Production of SO_2.

B. Conversion of an SO_2-O_2 mixture into SO_3 by means of a contact catalyst as opposed to a chemical one.

C. Production of sulphuric acid from SO_3.

Any plant which does approximately this is a contact process plant, and of course also has the equipment to perform many steps auxiliary to these. The flow sheet shows the schematic arrangement in a typical American contact-process plant (Figure 22).

Production of Sulphur Dioxide. All of the contact catalysts are sensitive to poisoning by impurities which stop their operation, platinum especially so, hence it is imperative that a good quality of SO_2 gas be supplied. In practice this requirement means that one is either limited to sulphur as a raw material, or else committed immediately to a preliminary purification installation that may cost an appreciable fraction of the total cost of the plant.

In the American process, Frasch-process sulphur is melted by means of steam, and then the molten sulphur is burned in sulphur burners in a draft of filtered and dried air. After removal of the heat of reaction in air coolers and filtration, the gases are ready for conversion. The waste heat at this and all points is recovered.

Where pure sulphur is not used as a source the burner process is followed by cooling and a complicated process of purification. In the Mannheim process using ferric oxide as a catalyst, however, the hot gases directly from the burners, may be passed through towers packed with the catalyst which is not so sensitive to impurities. A usual purification scheme might include successively:

A. The gases are cooled in a cooling tower.

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[3] Holmes, *General Chemistry*.

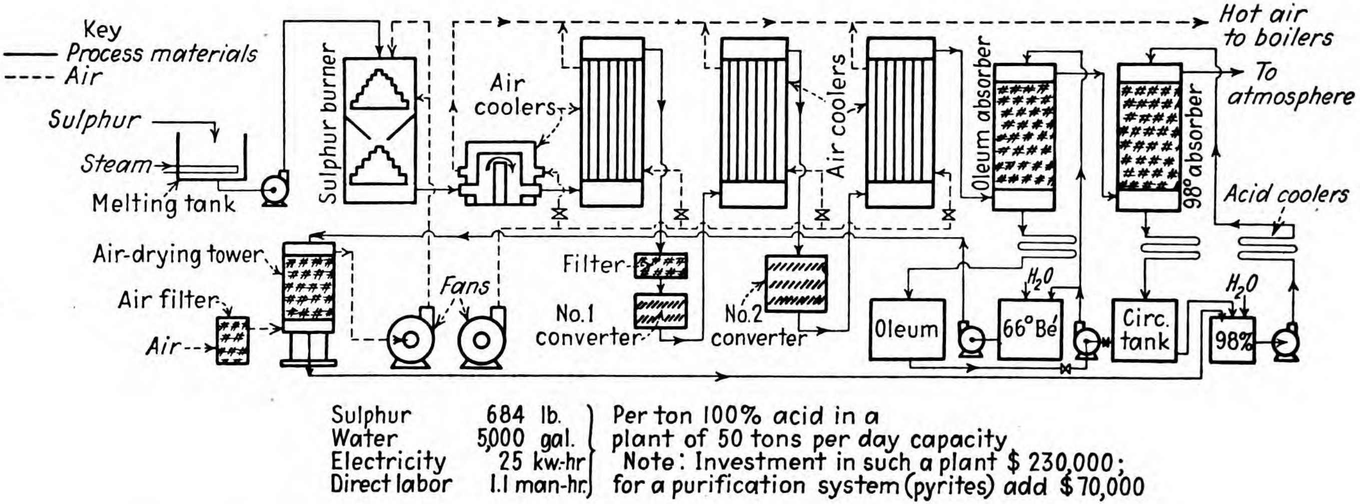


FIGURE 22: **Sulphuric Acid (Contact Process). Raw Gas-Brimstone Plant, Vanadium Catalyst**

(Courtesy of *Chemical and Metallurgical Engineering*)

B. They pass through a scrubbing tower where they are washed with cold sulphuric acid.

C. They pass through another tower where they are washed with very dilute sulphuric acid or dilute alkali to remove traces of chlorine and fluorine.

D. They are passed through a series of filters which consist of large rectangular boxes (30 feet by 30 feet by 1 foot) of sheet lead packed with finely divided coke.

E. The gases are passed through a tower lined with acid resisting brick, and in which circulates pure 95% sulphuric acid, which dries them thoroughly.

F. They are passed through another set of coke filters similar to the first, to remove any mechanically carried spray.

G. They pass through the blowers which create the draft for the whole cycle and are ready for conversion.

The Production of SO_3. The properly cooled and purified burner gases are converted into SO_3 in the converters. The converters are large cast-iron or steel boxes which contain the catalyst on shelves or trays. Formerly, electrically heated platinum gauze was used in the contact chamber. Platinum gauze is now replaced by other catalysts, and the converters are usually in pairs. The reaction is exothermic, and the heat of reaction is utilized by heat interchanger pipes between the contact chambers which heat the fresh cold gas, so that no heat is required to maintain the required temperature.

The catalyst on the shelves may be:

A. Platinum deposited on the surface of calcined magnesium sulphate in the Grillo process. This greatly reduces the amount of platinum required.

B. Platinum deposited on the surface of asbestos fiber in the Badische, Tentelew, Mannheim, and some American processes.

C. Platinum deposited on silica gel, in some American processes. This still further reduces the amount of platinum.

D. Vanadium pentoxide, V_2O_5, without or with such "promoters" as iron oxide and potassium compounds, in the United States.

E. Ferric oxide, Fe_2O_3, without or with CuO.

The gas entering the contact chamber contains by volume about 7% SO_2, about 13% oxygen, and the remainder—nitrogen and the other components of air—is colorless and has a strong odor of sulphur dioxide. The gas leaving the chamber is a dense white cloud of SO_3, which is comparatively odorless, although strongly acidic.

The temperature maintained in the chamber depends upon the catalyst. On theoretical grounds, the optimum temperature is below 400°C. for a better than 99% yield, but for catalysis it is always necessary to work at higher temperatures to secure maximum efficiency of the catalyst. The temperature of maximum efficiency for platinum is about 425°C., for V_2O_5 500°C., where its efficiency is higher than platinum, and for Fe_2O_3 about 625°C. At 625°C., even the maximum efficiency of Fe_2O_3, 50%, cannot be high theoretically, and so its use is followed up by the use of platinum to complete the reaction. In practice, with platinum, relatively little catalyst is required to convert 80% of the SO_2 to SO_3, while the other 20% requires relatively more, and by using two platinum steps the amount of catalyst can be still further reduced.

Up to the contact chambers, lead-lined materials can be used for interior plant construction. In the contact step and beyond, cast iron or steel or other resistant material must be used, as the strong acid corrodes lead rapidly.

The Production of Sulphuric Acid. From the converters the gases are again passed through air coolers, with utilization of the waste heat. They then go to the bottom of the oleum absorber towers. These are large cylindrical steel towers loosely packed with quartz, down which flows a stream of 98% sulphuric acid, which meets the up-going gas and absorbs the SO_3 to form oleum or fuming sulphuric acid. There are other methods of carrying out this step. In the process as pictured, the gases first pass through one tower containing an oleum absorber which produces a strong fuming acid that is cooled and run to storage. Part of this is diluted to 66°B. (99%) and some is used in a preliminary drying operation and in further absorption in the oleum tower. The gases from the first tower pass into a second similar tower where they meet a downcoming stream of 98% absorbing acid, and are absorbed to form a weaker oleum, which is cooled and passed into a circulating tank, from which part is diluted again to 98% for further use as absorbent in the second tower. After this step the gases are discarded.

The great merit of the contact process is that it produces sulphuric acid directly and by an economical procedure, at any desired strength from the strongest fuming acid—which may be obtained immediately—to the weakest. The strongest is produced first and all others obtained by the simple process of dilution. Both processes are, however, carried out on a large scale and individual plants of both types with a daily capacity of 1,000 tons are in operation. The outstanding disadvantages of the chamber process are the large space required and the relatively weak acid directly produced. The only serious problem of the contact process is the purity of the gas required. In their early days there was severe competition between the two, with the advantage all in favor of the contact process. A variety of factors have combined to change that situation—cheap pure sulphur as a source of pure SO_2, improvements in the chamber process (also, by the way, in the contact process), increasing cheapness of transportation which changes the relation of rental and location, very large demand for sulphuric acid of a wide range of concentrations, and others. It is somewhat true today to regard the contact and chamber processes as complementary rather than alternative procedures.

Chemistry of the Contact Process. The essential chemistry of the contact process is adequately represented by the equation already given:

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 + 45{,}200\ \text{calories}^{15^\circ C}.$$

or

$$SO_2 + \tfrac{1}{2}\ O_2 \rightleftharpoons SO_3 + 22{,}600\ \text{calories}.$$

While it is of considerable interest to determine the exact mechanism of the reaction, most of the important practical considerations are inherent in that equation, and the problems are largely physicochemical ones.

Thus by the usual principles of chemical equilibrium one should infer at once that the formation of SO_3 would be favored by a relatively high pressure and as low a temperature as possible and that the presence of inert materials in the reactants—for example, nitrogen from the air—is undesirable. Of these optimum condition predictions, practice regards seriously only the second. Since at ordinary temperatures the reaction proceeds so slowly as to be of little value, one therefore naturally seeks a catalyst which will accelerate the speed of attaining equilibrium, and whose maximum efficiency will be attained at as low a temperature as possible.

By the Law of Mass Action:

$$\frac{p_{SO_3}}{p_{SO_2} \times (p_{O_2})^{1/2}} = K_p$$

At 700°C., $K_p = 3.68$ for pressures in atmospheres.

For an increase in pressure, the fraction of $SO_3 \propto p^{1/2}$; and hence, for practical purposes, only relatively large changes in pressure would make great differences in efficiency. In practice, therefore, the economy of conduct at atmospheric pressure is considered to offset the advantage to be gained. Similarly for dilution with a relatively large volume of an inert gas, as nitrogen from the air, the fraction of SO_3 varies with $\frac{1}{d^{1/2}}$, where d is dilution. This effect is not relatively great and is not considered sufficient in the face of the principal factor to warrant the use of absolutely pure sulphur dioxide and oxygen. Both effects are, however, appreciable. Thus, taking the composition of burner gas as given earlier—SO_2 7%, O_2 13%—it may be calculated from the equation just given that at 700°C., p_{SO_3} is about .035. From the equation at equilibrium for pure SO_3 under these conditions, p_{SO_3} would be 0.50, which represents an efficiency, by calculation again from the equation, of 60% if the equilibrium is considered to represent the formation of SO_3 from the pure components. Now if all the SO_2 in the burner gas were converted into SO_3, the resulting p_{SO_3} would be .072. The reaction efficiency under these conditions actually is therefore

$$\frac{.035}{.072} \times 100 = 49\%;$$

that is, there is a loss in efficiency of 11% due to dilution, partially compensated by excess oxygen.

The value of K_p at different temperatures may be calculated theoretically from the Nernst equation:

$$\log K_p = \frac{Q_p}{4.581} + n\,1.75 \log T + nC,$$

where n (from the equation, p. 171) is $2 - 2 - 1 = -1$ (or $-\frac{1}{2}$). C is the conventional chemical constant for the gases involved, and may be obtained from a handbook or calculated from any one value on the graph (Figure 23). Actually, the variation in K_p is represented approximately, Figure 23, of which three points are $K_p^{400°C.} = 1{,}410$, $K_p^{700°C.} = 3.68$, $K_p^{900} = .018$.

In terms of chemical theory, no catalyst can produce a yield exceeding the yield, calculated from K_p obtained from this equation, at any given temperature. However, at temperatures where in practice equilibrium is never attained because of the slowness of the reaction, a suitable catalyst may enable the equilibrium to be reached almost immediately because of its effect in accelerating the reaction.

Most catalysts begin to exhibit some activity at fairly low temperatures, in terms of a yield better than that in their absence. As the temperature rises, the yield increases to a maximum which may approach the theoretical and then diminishes beyond the temperature of the maximum. Platinum has its maximum at about 425°C., V_2O_5 around 500°C., and both give nearly theoretical yields, although V_2O_5 is a little better. Fe_2O_3 has its maximum around 550°C., but its efficiency is only about 50%. In the case of the oxide catalysts, a trace of another oxide may greatly promote efficiency, and these addenda are known as promoters. CuO is a promoter for Fe_2O_3, and Fe_2O_3 and other materials for V_2O_5. On the other hand, very small traces of certain impurities in the gases, especially arsenic compounds and halogens, will completely inhibit the action of the catalyst, which is then said to be poisoned. Different catalysts vary in sensitivity to poisoning. Physical form of the catalyst, especially surface, affects its efficiency greatly. The study of catalysis is an extensive and complex field, and the studies of the contact process have contributed greatly to it.

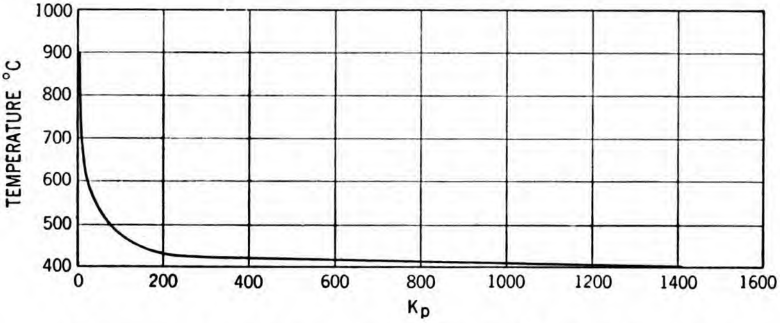


FIGURE 23: K_p—**Temperature curve for** $SO_2 + \frac{1}{2} O_2 = SO_3$

Another interesting aspect of the chemistry of the contact process is the fact that although SO_3 is readily soluble in water, under the condition in which it is prepared in the process it can be bubbled through water successively many times without solution, and must be absorbed in strong sulphuric acid. This fact can be clearly demonstrated experimentally by setting up a horizontal hard glass tube containing a piece of platinum foil at its center which can be heated from the outside by a gas flame. A mixture of SO_2 and oxygen is passed over the heated platinum and then the gases are passed successively through several gas bubbler bottles containing water and finally one containing concentrated sulphuric acid. The smoky cloud of SO_3 containing gas is clearly seen going through the water, and then disappears in the acid. The effect is a colloidal one.

Sulphuric Acid, H_2SO_4. The sulphuric acid prepared by the contact process is purer than that from the chamber process. Pure sulphuric acid, H_2SO_4, which is also known as monohydrate, and "oil of vitriol," is a colorless liquid, which contains 100% of the compound and has a specific gravity of 1.831 at 20/4°C. It begins to boil with decomposition at 270°C., to form a constant-boiling mixture at 338°C. which contains 98.33% of acid. Mixtures of the acid with water have a generally increasing specific gravity with increasing concentration, but the aqueous solution exhibits a maximum specific gravity of 1.836 at about 97% strength (see Figure 24). The strength of sulphuric acid is obtained by the Baumé hydrometer calibrated for 60/60°F., and strength tables are given in the Appendix.

$$°\text{Baumé} = 145 - \frac{145}{\text{specific gravity}}$$

Acids stronger than 66°B. have their strength determined by chemical analysis, which of course might be used for any.

The familiar commercial forms are:

A. Various dilute acids, such as battery acid, specific gravity 1.2.

B. Commercial concentrated, 95% to 100%.

C. Monohydrate, useful in explosive work, 100%.

D. Oleum, Nordhausen, or fuming sulphuric acid.

This last is 100% sulphuric acid containing an excess of SO_3. The excess SO_3 is probably present at least in part as pyrosulphuric acid, and possibly other compounds, but is merely designated, for example, as 20% fuming sulphuric, which is a solution containing 80 grams of monohydrate and 20 grams of SO_3. It can be made up to 65% or more fuming. The familiar grades are 20% and 60–65%, both of which are liquid at ordinary temperatures, while from 20% to 60% and above 65% they are solid.

Sulphuric acid is commonly sold in 10-gallon glass carboys, and in steel drums or steel tank cars. Only acid at greater than 75% strength can be kept in steel containers. Above 75%, sulphuric acid is very weakly acidic and is a powerful dehydrating agent, which is its explosive use, and when heated is a fair oxidizing agent. The dilute acid is a cheap, strong acid.

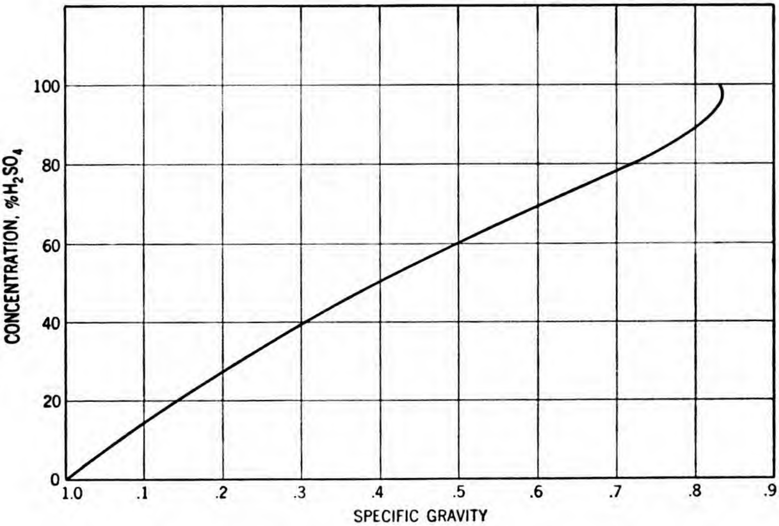


FIGURE 24: **Sulphuric Acid**
Specific-Gravity Composition of Aqueous Solutions

Purity of Sulphuric Acid. It is important that sulphuric acid for explosives work be free from at least certain types of impurities. Suspended solids, as for example $PbSO_4$, may exert an emulsifying effect in mixed acid which may greatly hinder rapid separation. Organic material, if it gets into the acid by careless handling, may produce aliphatic nitro compounds during nitration—such as tetranitromethane, which is readily formed in traces from almost anything—and these may give the resulting explosive an apparently very poor Abel or KI test, when it really rates better.

Sulphuric acid is analyzed for strength as given, and then for lead, iron, arsenic, antimony, zinc, copper, selenium, and total residue on evaporation.

Other Methods of Making Sulphuric Acid. There are other methods for making sulphuric acid which have potential or actual commercial application. Chlorine gas can be used to replace oxides of nitrogen, in a modified chamber process. The mechanism is possibly:

$$2\ Cl_2 + O_2 \rightleftharpoons 2\ Cl_2O,$$

$$SO_2 + H_2O + Cl_2O \rightleftharpoons H_2SO_4 + Cl_2,$$

and so on.

Sodium sulphate can be electrolyzed to produce sulphuric acid, in a cell similar to the Nelson or the Vorce cell used for electrolytic sodium hydroxide.

$$Na_2SO_4 + 2\ H_2O \rightleftharpoons 2\ NaOH + H_2SO_4.$$

This reaction, which is commonly regarded as being too expensive because of the high cost of electric power in the United States, is said to be used on a large scale in the U.S.S.R.

Discussion Questions and Exercises

1. What other strictly chemical substance rivals sulphuric acid in tonnage figures?

2. Tabulate and compare all of the advantages and disadvantages of the chamber and contact processes.

3. Report on the chemistry of the system H_2O-H_2SO_4.

4. Discuss the proposition, "Catalysis never causes a reaction to occur which does not take place by itself," in the light of any apparently contradictory chemical facts you can find.

5. Report on "Catalysis."

6. Prepare sketches, including dimensions, of important parts of the sulphuric acid processes machinery.

7. Examine the sources of waste heat in these processes and discuss methods of recovery and use.

8. Calculate the value of C in the Nernst equation.

9. Set up carefully a K_p curve similar to the one in Figure 23, but covering only the temperature range of the useful catalysts.

10. Find out present costs of the different concentrations of sulphuric acid in commercial quantities.

11. Prepare an outline for a complete analysis of sulphuric acid.

CHAPTER 10

Nitric Acid, the Fixation of Nitrogen, and Ammonium Nitrate as an Explosive

Nitric Acid, HNO_3. This acid was first described by Geber, and later became known as aqua fortis. A mixture with hydrochloric acid was also discovered early and named aqua regia because of its ability to dissolve gold. The modern process of preparing nitric acid by the distillation of a mixture of sodium nitrate and sulphuric acid was discovered by Glauber. Preparation of nitric acid by this or any similar procedures, without other precautions, does not yield a pure nitric acid, but rather one which is pale yellow to brown owing to decomposition at its boiling point, with absorption of the oxides of nitrogen according to the equation:

$$4\ HNO_3 \rightleftharpoons 2\ H_2O + \uparrow 4\ NO_2 + \uparrow O_2.$$

The decomposition is, however, only about 1% or 2% and with anhydrous materials the Glauber process yields a very strong acid.

Pure nitric acid may be prepared by bubbling air containing NO_2 through the acid, or better by distillation over a mixture of barium and silver nitrate, followed by distillation under diminished pressure over urea. This procedure removes, besides other impurities, sulphate, halogen, and lower oxides of nitrogen, as well as water. The use of greatly diminished pressure avoids the decomposition at the normal boiling point.

Pure nitric acid, or monohydrate, 100%, is a water-white liquid, specific gravity 1.54, boiling point with decomposition 86°C., and melting point −47°C. The monohydrate consists, according to Hantsch, of "nitronium" nitrate, $N(OH)_3\ (NO_3)_2(=[HNO_3]_3)$. Decomposition continues on boiling to a composition of 68% HNO_3, which is the constant-boiling mixture (boiling point 120.5°C.) and is also the commercial concentrated nitric acid; it has a specific gravity of 1.411. The specific gravity of nitric acid increases with concentration and does not show a maximum, as does that of sulphuric acid (see Figure 25). The strength up to 48.5°B., 95.11%, which is the strongest usual commercial acid, can be determined with the Baumé hydrometer, and strength above that by analysis. A nitric-acid table is given in the Appendix.

Nitric acid is characterized by the reaction with organic materials which makes it useful for explosive work, and it acquires this property at lower concentrations as the ease of nitration increases. It is also a strong acid at all concentrations, although the strength diminishes markedly with increasing concentrations. It is likewise a strong oxidizing agent at all concentrations. It will oxidize all of the common metals except gold and platinum and will also dissolve them, since all of its simple salts are soluble. Its oxidizing power in general increases with increasing concentration, but the oxidation-reduction equilibria are complicated and present an interesting problem which has been extensively worked out.

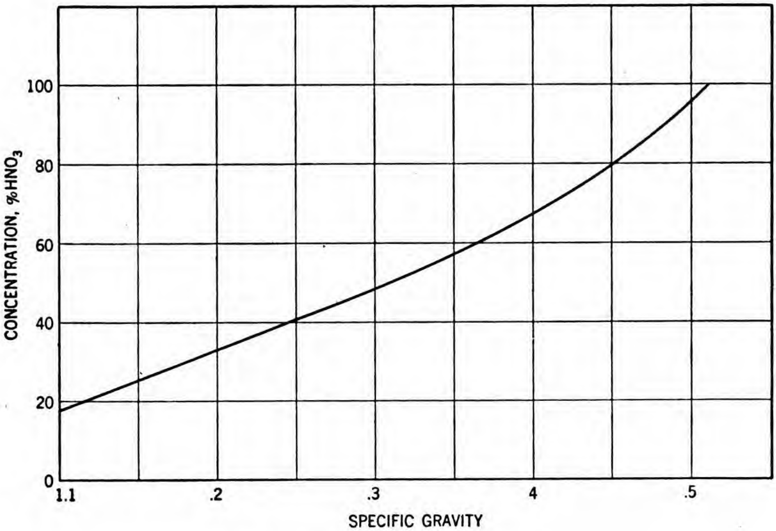


FIGURE 25: **Nitric Acid**
Specific-Gravity Composition of Aqueous Solutions

Nitric acid and nitrates are readily detected by the "brown ring" test, and the formation of a deep blue color on reaction with metallic copper in the presence of sulphuric acid followed by neutralization with ammonium hydroxide. These tests do not distinguish nitric acid from nitrites and nitrous acid, but this is readily done by reference to the stability and lack of reducing properties of nitric acid. Strong nitric acid exhibits the xanthoproteic reaction.

The usual commercial forms of nitric acid are:

A. Various dilute acids, which are of little use in the explosive field.

B. Commercial concentrated nitric acid, 68%. Even this grade is too dilute for making up most mixed acids.

C. Highly concentrated commercial acid, 93% to 95%. This grade is the one extensively used in the explosive industry, and is sometimes called fuming nitric acid.

D. Fuming nitric acid. This grade is concentrated nitric acid containing excess NO_2. It is little used anywhere, although the acid in (*C*) is sometimes referred to as fuming nitric acid; if carelessly prepared, it is a fuming acid. The presence of more than traces of free oxides of nitrogen in mixed acid is objectionable in explosives work because of the side reactions that may occur between organic compounds and nitrous acid, and also because the corresponding nitrite would in general be more unstable than the desired compound.

Nitric acid is sold in 10-gallon carboys, and in larger vitreous-finished containers, although there are metallic alloys which will withstand its action.

Manufacture of Nitric Acid. The cheapest and usual method of manufacture is the straight distillation of a mixture of Chile niter with sulphuric acid. In practice, iodine is recovered as a by-product in this reaction unless the niter is subjected to a preliminary purification.

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

The materials are fed into horizontal cast-iron or duriron (16% Si) stills and heated; the vapors are let out by glass tubes and condensed in earthenware vessels, a process which in substantial form has changed little since the earliest days. The mixture is not made up in the proportion indicated by the equation (about 1:1), because under those circumstances the residue would be solid and difficult to remove from the stills. An excess of sulphuric acid is employed sufficient to keep the mass liquid at the temperature of operation, although it solidifies on cooling, and is known as "niter cake." Since at least two pounds are obtained for every pound of nitric acid produced, it is a potentially valuable by-product obtained in enormous quantities, and the development of uses for it has been large, successful, and interesting.

The actual distillation may be carried out in a variety of ways:

A. Using concentrated sulphuric acid, a temperature around 110° to 130°C., and atmospheric pressure, the product obtained is a strong nitric acid, 90% to 95%, containing free oxides of nitrogen—"fuming nitric acid." By redistilling and bubbling air through the product, the oxides of nitrogen may be removed.

B. Using concentrated sulphuric acid at a slightly reduced pressure which reduces the boiling temperature, and yields a strong acid (93% to 95%) with small amounts of oxides of nitrogen, or more.

C. Using a properly diluted sulphuric acid, which by regulated heating will yield commercial concentrated nitric acid, 68%, with almost no decomposition.

Purity of Nitric Acid. Apart from any introduced by carelessness in handling, the only impurities which nitric acid is likely to contain that are objectionable from the standpoint of explosives manufactur? are nitrous acid and oxides of nitrogen. These may be detected and quantitatively estimated by using diphenylamine. The strength of nitric acid is estimated as previously given, and it is commonly analyzed for sulphates, free chlorine, iodine, halogens in general, and total residue on evaporation.

The Fixation of Nitrogen. The usual annual American production of nitric acid by the distillation process is about 100,000 tons. To produce a pound of explosive, as has been seen, uses about 1½ pounds of nitric acid. Many other important chemicals of commerce are also nitrogen compounds, many start with nitric acid and the process of nitration, and all of these require nitrogen compounds as starting materials. Among them may be mentioned—in addition to explosives—fertilizers, dyes, plastics and resins, pharmaceuticals, narcotics and medicinals, photographic chemicals, and fine chemicals in general. Modern civilization is to a large extent dependent upon these materials. The present population in the world could not be fed, even at its present not altogether satisfactory level, without the use of nitrate fertilizer, among others, on a large scale. The production of nitric acid may be cheaply expanded to any desired figure, using Chile niter, for the deposits of this material alone are competently estimated to be capable of supplying the needs of the world for more than 1,000 years; such estimates, moreover, in general prove to be low rather than high. But in view of the mischances of the modern world, war for example, it is a serious risk for the United States to depend largely on so remote a source as the Chilean beds for such imperative necessities.

Speculation of the above sort, given further impetus by other considerations, led in the last quarter of the nineteenth century to efforts to make useful nitrogen compounds from the free nitrogen of the atmosphere. The difficult problem is to make free nitrogen combine; once it is combined it is comparatively simple to make any compound from any other. This problem became known as that of the "fixation of nitrogen." It has, in the since intervening period, been solved in a variety of ways. Some of them yield nitric acid directly, and all can yield it ultimately, so fixation processes are an important commercial source of nitric acid.

There is, however, within most countries another large source of nitrogen. This is the so-called "by-product ammonia" recovered from the gases obtained by the distillation of coal to make coke or fuel gas. On washing the gas with sulphuric acid, the ammonia is recovered as $(NH_4)_2SO_4$, and it is estimated that about one million tons of this could be made available in the United States annually at present. This recovered ammonia can be and is converted to nitric acid by the Ostwald process, and this process is the third important commercial source of nitric acid.

These considerations are also closely related to an important political and military problem in the United States. In war times, the use of explosives increases enormously, experts disagree on actual needs at present. One would be inclined to say that at this date all estimates have been too low, and that a nation like the United States, for safety, should have a potential explosives capacity of more than 5,000,000 tons annually. For this, organic material, sulphuric acid, and nitric acid would be required in the quantities now familiar to us. The first two needs present no serious difficulty, although the diversion of the necessary quantities might cause a certain amount of industrial dislocation. However, nothing like the necessary quantity of nitric acid is anywhere in sight in the United States. The fixation of nitrogen is a present practical problem as well as a past chemical one, and we shall be fortunate if we do not suffer from our failure to give it more attention.

The Arc Processes: The Berkeland-Eyde Process. The first practical nitrogen-fixation process was this one. Its early history is the subject of some dispute. Patents seem to have been taken out by Madame Lefebre (1859) and McDougall (1899). It went into commercial production at Notodden in Norway (1904) as the result of the work of the two Norwegians whose names the process bears, but seems to have been operated to some extent in the United States in 1903 by Bradley and Lovejoy, who took out patents in 1901.

The basic materials used are air and water, and the essential reactions are:

$$N_2 + O_2 \rightleftharpoons 2\ NO - 43{,}200 \text{ calories} \tag{a}$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 + 28{,}400 \text{ calories} \tag{b}$$

$$3\ NO_2 + H_2O \rightleftharpoons 2\ HNO_3 + NO \tag{c}$$

Reactions (b) and (c) present no difficulty; they take place at ordinary conditions on contact. Reaction (a) is a problem. Nitrogen and oxygen do not combine at ordinary temperatures. A high temperature favors the formation of NO but at 2,000°C. combination is 1% and at 3,000°C., 5%. This temperature is brought about by the use of an electric arc, and the gas mixture must be cooled as quickly as possible to prevent decomposition of the product in the cooling range where equilibrium would tend to be rapidly established. Pressure is not a significant factor since there is no change in volume, and air is an almost ideal starting material from the standpoint of composition. The yield of nitric oxide from electric-arc fixation is almost twice as great as the chemical theory predicts for the temperature of the arc, and seems to indicate that the arc has more of an effect than merely heating.

In the original process, an arc was struck between two carbon electrodes inclined at an angle to each other. A vertical blast of air blew the arc up the electrodes, and the reacting air was blown in a horizontal direction through the triangular sheet of flame thus formed.

In modern practice an arc is struck between two horizontal water-cooled copper electrodes. A powerful alternating-current electromagnet, with its poles perpendicular to and on either side of the arc, blows it into a circular sheet of flame several feet in diameter, half of which is extinguished at every cycle of the current. The time of contact between air and flame is thus further reduced. The process has a number of variations. The Schonherr process uses an arc in a vertical tube; the air passes up this tube and then down through an outer jacket, thus heating the incoming air. The Paulling process, used in 1917 in the United States, employs an arc in a diminishing helical form.

After leaving the arc, the air contains not over 7% nitric oxide, so combination with additional oxygen to form NO_2 occurs on cooling. This reaction can be illustrated for lecture purposes by striking an arc between platinum points in a closed flask of air by means of an induction coil. The flask soon becomes perceptibly brown.

The gases from the electric furnace are cooled, the waste heat recovered, and the cool gases brought into contact with water in one of the usual types of countercurrent towers, where reaction (c) takes place and a rather weak nitric acid is formed, which may, however, be concentrated. From the equation it is evident that water does not absorb all the gas, and the residual oxides of nitrogen can be absorbed in soda ash solution from which sodium nitrate and nitrite can be recovered. This recovery, however, may be avoided.

The electric-arc fixation process is ordinarily expensive in electricity in most places, and while still in use, is not in favor for new plants.

The Cyanamid Process. This process takes its name from the intermediate product $CaCN_2$, calcium cyanamid. It was originally developed by the Germans, Frank and Caro, and was introduced into the United States in 1907 by the American Cyanamid Company, which has operated and improved it continuously ever since. The raw materials are principally limestone, coke, and pure nitrogen, which is prepared as a preliminary operation from air. The essential chemical reactions are:

$$CaO + 3\ C \rightleftharpoons CaC_2 + CO \tag{a}$$

$$CaC_2 + N_2 \rightleftharpoons CaCN_2 + C \tag{b}$$

$$CaCN_2 + 3\ H_2O \rightleftharpoons CaCO_3 + 2\ NH_3 \tag{c}$$

The quicklime is made by burning limestone by the usual procedure. The mixture of lime and ground coke is put into an electric furnace of the arc type using heavy graphite electrodes, and heated to form calcium carbide.

Reaction (b) is likewise an electric-furnace operation, although the heating is not as great. The furnace (cyanamid ovens) is of the resistance type, and cylindrical in shape, a relatively thin graphite resistance unit running vertically down the center. Ground calcium carbide is packed around the pencil to fill the furnace. Pure nitrogen is prepared from air, in the United States usually by large liquid-air units. It may also be made from air by gas reactions, which will be described in connection with the Haber process. The furnace is allowed to begin to heat up and nitrogen—which must be fairly pure (99.8%)—is introduced at the bottom around the electrode. The reaction is exothermic and once it begins it spreads through the mass; further electrical heating is then unnecessary. The reaction is catalyzed by impurities which are present in the impure material, as pure CaC_2 does not react readily with nitrogen. In a plant, these ovens may be many in number, arranged in long rows. The reaction takes 24 hours or more for completion, after which the solid mass of oven contents is removed in solid blocks by overhead traveling cranes, and ground. This product may be used as a fertilizer and for other purposes. It contains, in general, $CaCN_2$ 60%; lime 20%; carbon, 12%; impurities of Fe_2O_3 and Al_2O_3; and has about 21% available nitrogen.

Reaction (c) is carried out in steel-jacketed autoclaves heated by steam under pressure and results in the formation of ammonia. A great many products may be made in a cyanamid plant, but it is usually operated in conjunction with an Ostwald-process installation for the production of nitric acid from ammonia. This process, which bears the name of Wilhelm Ostwald and appeared in Germany in 1913, seems nevertheless to have been simultaneously evolved in the United States by the American Cyanamid Company and is an important method of making nitric acid. The Cyanamid Process is also used in Germany to some extent.

The Ostwald Process. The essential reactions of the Ostwald process (see Figure 26) are:

$$4\ NH_3 + 5\ O_2 \overset{Pt}{\rightleftharpoons} 4\ NO + 6\ H_2O + 214{,}600 \text{ calories} \tag{a}$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 \tag{b}$$

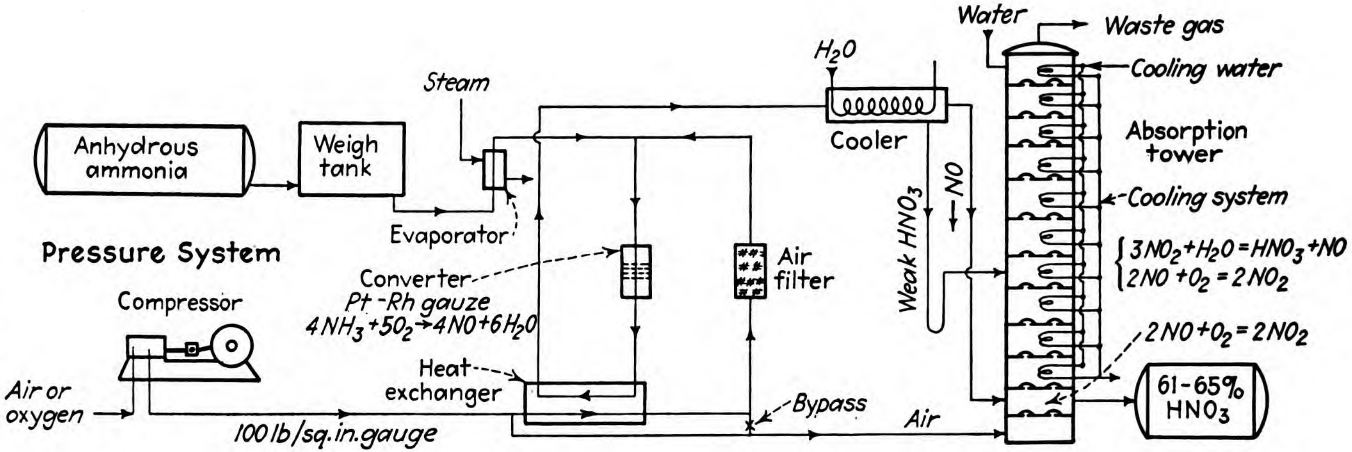
$$3\ NO_2 + H_2O \rightleftharpoons 2\ HNO_3 + NO \tag{c}$$

Reactions (b) and (c) need no further comment.

Reaction (a) requires a catalyst, for when ammonia is merely burned in air it yields largely water and nitrogen. Kuhlman (1839) found that platinum would serve. The reaction is exothermic and once it is initiated can be made to maintain itself, as can be readily demonstrated by passing a mixture of ammonia and air over a piece of platinum foil in a horizontal hard glass tube. The platinum must be heated but when the reaction starts it begins to glow; from that point, the heat may be turned off and a red glow maintained by properly regulating the gas flow.

Ammonia, from any source but carefully dehydrated, is mixed with about 10 volumes of air, or with a smaller volume of air enriched by the addition of oxygen, or with pure oxygen. The mixed filtered gases are preheated and passed through the contact chamber. This is in essentials merely a box containing four separated layers of platinum, or platinum-rhodium gauze, which may be electrically heated, although the reaction maintains itself. The gauze is 80–150 mesh per inch, wire diameter 0.001–0.003 inch, and becomes more efficient after use as the surface changes. Two square feet of gauze will catalyze a production of about 1.5 tons of 100% HNO_3 per 24 hours for three months. The temperature is 650° to 1,000°C. and the time of contact, which is important, is about 0.0001 second. A yield of about 95% to 98% of NO from the ammonia is obtained. Some promoted oxide catalysts, such as Fe_2O_3, may be used. Impurities in this process may also poison the catalyst.

The cooled gases from the contact chamber are brought to the bottom of a countercurrent absorption tower. At the top of the tower water is admitted, and further down, nitric acid which has condensed from the cooling of the contact gases. At the bottom of the tower the contact gases are mixed with air in a proportion sufficient to allow for further reconversion of NO to NO_2 within the tower. Reactions (b) and (c) take place in the tower and with proper regulation the



Anhydrous ammonia	590 lb.
Platinum	Variable
Power	470 Kw.-hr.
Direct labor	2.7 man-hr.

In some plants, Pt loss is about 0.012 oz. per ton

Per ton 100 per cent HNO_3
Reference on pressure synthesis: Taylor, Chilton and Handforth, Ind. Eng. Chem., Vol. 23, p. 860 (1931)

FIGURE 26: **Ostwald Process for Nitric Acid**
(Courtesy of *Chemical and Metallurgical Engineering*)

gas at the top may be discarded. The acid produced is about 63%. In the Fauser process in Italy a different method of absorption is employed. A chrome-steel alloy is fairly resistant to nitric acid and may be used for construction.

When, as is usual, the Ostwald process is employed in conjunction with the cyanamid process, or the Haber process, it is customary to convert to nitric acid half or more of the ammonia formed by this method. The remainder of the ammonia is absorbed in water in countercurrent absorption towers. The acid from the Ostwald process and the ammonia solution from the tower are then run into thickeners, where they react to form ammonium nitrate:

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3.$$

In the open cylindrical thickeners, which are essentially large tubs with stirrers, the solution is evaporated by steam, and continuously stirred for graining, which finally produces white, solid, granular NH_4NO_3 as the ultimate product. The entire production may consist of this.

The Haber-Bosch or Haber Processes. All of these processes are based essentially upon the reaction:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 + 24{,}000 \text{ calories.}$$

This reaction has been known since 1850, but the combination—not then clearly understood—of a reversible, exothermic reaction of great slowness at ordinary temperatures, with some unusual practical difficulties, was too much for the technical ability of the time. Only in 1913 did Fritz Haber by physicochemical study and Karl Bosch by engineering design make the process commercially workable. It has undergone continuous improvement since, and is the preferred method for new construction today.

Based on equilibrium considerations:

$$\frac{(p_{NH_3})^2}{p_{N_2} \times p_{H_2}^3} = K_p. \qquad \text{(a)}$$

We can say at once that, in general, optimum conditions would demand:

A. As high a pressure as practical.
B. As low a temperature as possible.

C. With the knowledge that no ammonia is detectable in the reaction mixture at ordinary temperatures, the requirement of a catalyst suggests itself.

D. Starting materials as pure as possible.

E. Hydrogen, preferably, in excess in the starting mixture.

A. Pressure. In a mixture from 2 moles of ammonia at constant temperature, let x = the fraction of a mole which exists as nitrogen at equilibrium, and let p = the total pressure in atmospheres. Then, by equation (a), p. 187,

$$\frac{\left[\left(\frac{1-x}{1+x}\right)p\right]^2}{\left[\frac{x}{2(1+x)}p\right]\left[\frac{3x}{2(1+x)}p\right]^3} = K_p,$$

or

$$\frac{16(1-x^2)^2}{27x^4} = p^2K_p.$$

It is therefore clear that in general the yield of ammonia varies as p^2, and from any value of K_p may be calculated theoretically, for any pressure. The percentage conversion in practice of a $N_2:3\,H_2$ mixture to ammonia is given in Table 30, as determined experimentally for one atmosphere and 200 atmospheres pressure. At 10 atmospheres the percentage conversion is still practically zero at 1,000°C. The pressure of 200 atmospheres represented in the early days about the upper limit of the apparatus strength and even so explosions

TABLE 30

CONVERSION OF $N_2:3H_2$ TO AMMONIA

Temperature, °C.	Percentage as NH_3	
	1 atmosphere	200 atmosphere
200	15.3	86.
300	2.2	
500	0.13	17.6
600	0.05	8.2
1,000	0.004	0.8

were frequent. Today, in the improved processes with modern materials, pressures up to 1,000 atmospheres are used with corresponding increases in yield.

B. Temperature. The figures just given indicate how the ammonia yield diminishes with rising temperature, pressure remaining constant. This yield may be calculated theoretically from the Nernst equation (p. 172), the equation on page 188, the heat of reaction, and any one value of K_p as previously indicated. The reaction is exceedingly slow (imperceptible) at ordinary temperatures, and even at elevated temperatures reaches equilibrium too slowly for practical value, except in a temperature range where the yield is prohibitively

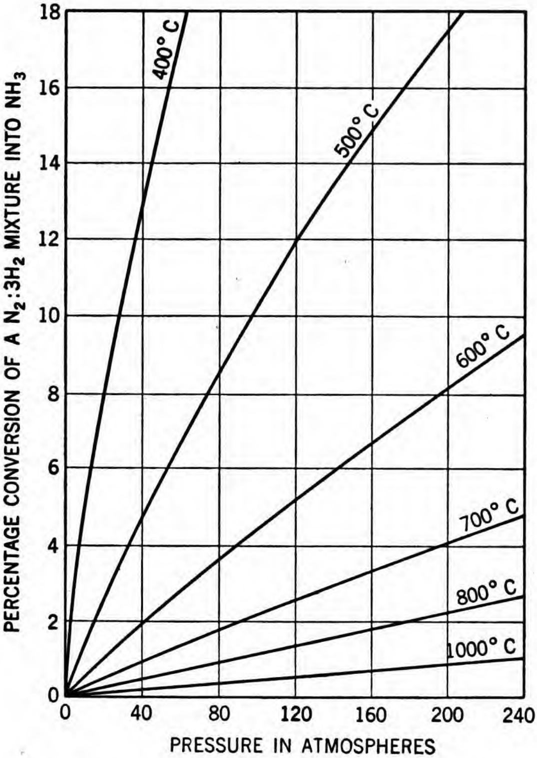


FIGURE 27: **Equilibrium Curves for the Haber Process at a Series of Constant Temperatures**

(Reprinted by permission from Kendall-Smith, *Inorganic Chemistry*, courtesy of D. Appleton-Century Co.)

low. With the best of catalysts, it takes more than four hours to reach equilibrium around 500°C., and this is the range of practical operation. The catalysts used in some processes may still be secret, but these will function: iron with molybdenum; osmium; uranium; ferric oxide promoted with oxides of aluminum, and potassium; ruthenium; nickel or iron with sodamide; and calcium ferrite. They present some aspects of the usual poisoning problem. The gases from the equilibrium mixture are recirculated after ammonia removal.

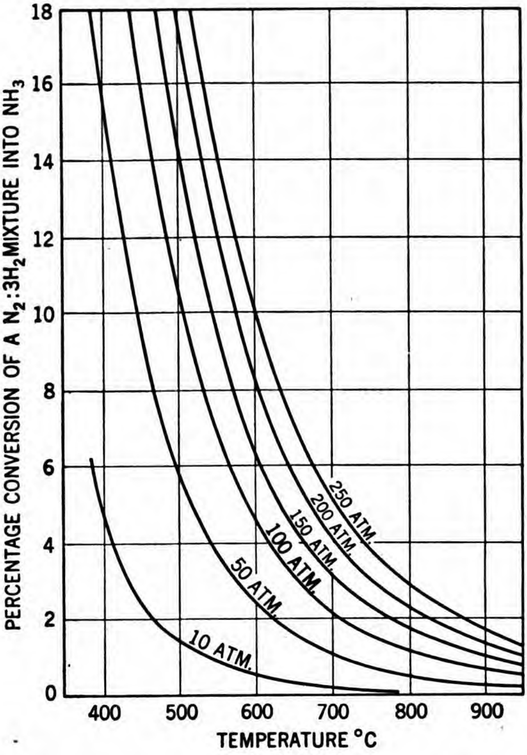
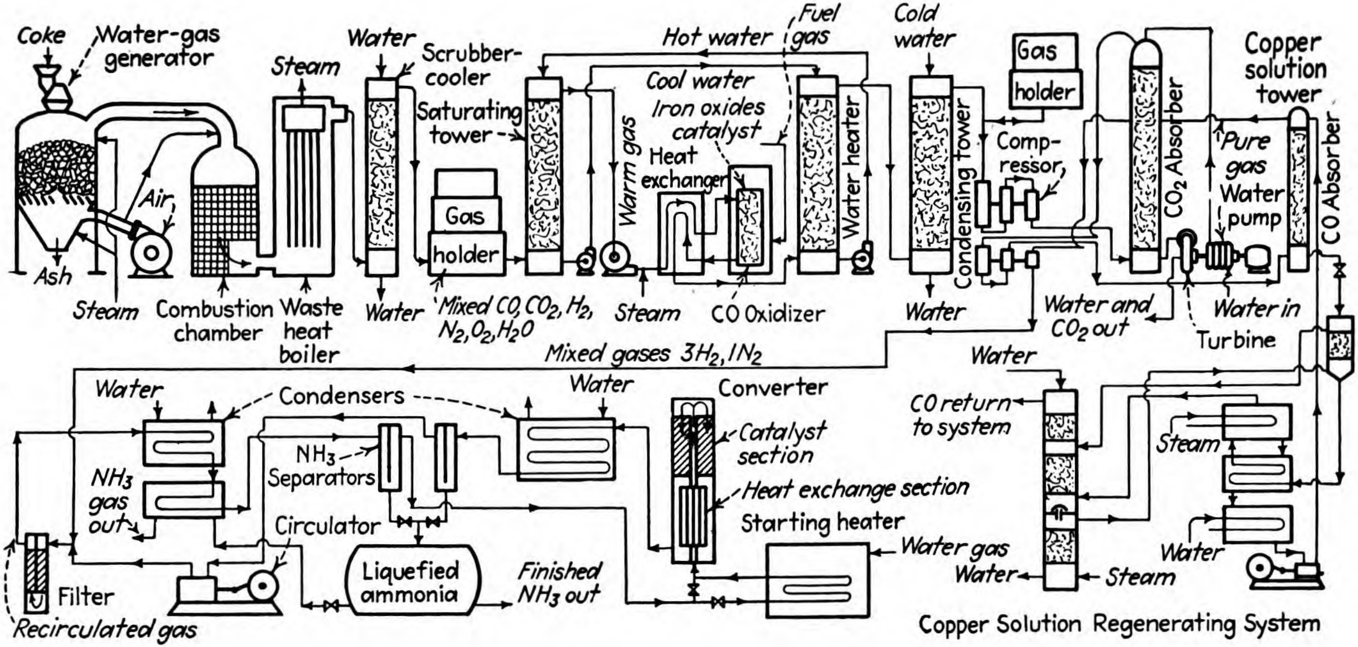


FIGURE 28: **Equilibrium Curves for the Haber Process at a Series of Constant Pressures**

(Reprinted by permission from Kendall-Smith, *Inorganic Chemistry*, courtesy of D. Appleton-Century Co.)

C. Other factors. The practical problem resolves itself into: (1) Adoption of working conditions based upon considerations such as the preceding. (2) Production of pure hydrogen and nitrogen. These



Coke	1.65-1.75	tons	Per ton liquefied NH_3
Water	31,000	gals.	
Coal (steam and power)	25	tons	
Direct labor (about)	20	man-hr.	

FIGURE 29: **Ammonia Synthesis (Nitrogen Engineering Corp. System)**
(Courtesy of *Chemical and Metallurgical Engineering*)

gases must be quite pure first because of possible poisoning of the catalyst. This danger is not as serious as in some cases, but carbon monoxide and sulphur compounds are especially objectionable, and the gases are treated to remove the final traces. Moreover, theoretic considerations indicate that the yield of ammonia varies inversely with the square of dilution (prove), so the presence of absolutely large quantities of otherwise unobjectionable diluents largely affects the yield. (3) Conduct of the main reaction. (4) Removal of the ammonia, and reutilization of the residual mixture.

In the past in the United States, nitrogen was largely obtained from liquid air, and electrolytic by-product hydrogen was desired because of its purity, although all of the usual hydrogen processes have been used. In Germany, all gas reactions have long been used, and the Badische procedure may be regarded as more or less the standard for most economical operation. In it hydrogen is prepared by the water-gas reaction from steam and coke,

$$C + H_2O \rightleftharpoons CO + H_2.$$

The carbon monoxide is selectively oxidized to CO_2 by mixing with steam and passing the hot gases over a suitable catalyst.

$$CO + H_2 + H_2O \rightleftharpoons CO_2 + 2\ H_2.$$

Here again, the catalyst may be unrevealed, but calcium oxide will function. Finally the CO_2 is removed from the mixture by passing the gases under pressure through water.

Nitrogen is obtained from air by what is substantially a modified producer-gas procedure.

$$5\ \text{air} + 2\ C \rightleftharpoons 2\ CO + 4\ N_2\ \text{approximately.}$$

With steam, somewhat similarly to the preceding reaction, selective oxidation may be achieved.

$$2\ CO + 4\ N_2 + 2\ H_2O \rightleftharpoons 2\ CO_2 + 4\ N_2 + 2\ H_2.$$

The carbon dioxide can be removed as before. The reaction may be conducted by mixing the water gas and producer gas to give a mixture containing about 22% nitrogen and then oxidizing the mixture with steam. Under these circumstances, Table 31 gives possible and approximate gas-mixture compositions.

These figures are not to be compared with ideal calculations because of the introduction of impurities from raw materials, and are not intended to check other than roughly with each other. Passage of the final mixture through water reduces CO_2 to 1% and the remainder is removed with alkali. Residual carbon monoxide and sulphur compounds must now be removed, treatment with cuprous ammonium carbonate or ammonia may be used, and the gas mixture is finally passed through molten sodamide and sodium. The gas may be allowed to remain in contact with a mixture of $NaNH_2$ 80% and Na 20% for 60 seconds at 225°C.

The purified gas mixture is now compressed, sometimes in stages, and passed into the contact ovens. These are steel ovens in which the gas remains several hours under the prescribed conditions. Special steels have been designed for these ovens and increasingly higher pressures are used. There are many modifications of the Haber process which differ in the pressure, the method of recovery of ammonia, and the method of circulating the residual gases after recovery of the ammonia. These modifications include the Claude process, where the ammonia liquefies under cooling at the pressure (up to 1,000 atmospheres) used; and the Casale process, at a slightly lower pressure where only part of the ammonia is removed before recirculating in order to prevent overheating of the catalyst.

TABLE 31

GAS-MIXTURE COMPOSITION

Gas mixture	Volume %				
	CO	H_2	N_2	CO_2	Others, not more than
Water gas	43	50			7
Producer gas	30		65		5
Mixture	35	33	22		10
Mixture after oxidation	2	52	17	27	2

The reaction in the contact chamber, which is electrically heated, is exothermic and once begun may require cooling rather than further heating. Most usually, after leaving the contact chamber the gases are reduced in pressure, the ammonia removed by absorption in countercurrent towers containing water, although the first part usually is removed by liquefaction on cooling before decompression and the residual gas is reused by adding it to the original mixture. There are, as has been indicated, many modifications of this procedure as well as many ingenious devices designed for heat recovery, conservation, and efficiency.

Like the cyanamid process, the Haber process is used in conjunction with the Ostwald process, so that its principal final products may be regarded as nitric acid and ammonium nitrate.

In summary the Haber process[es] produce[s] nitric acid and ammonium nitrate from water, air, coke, and power, and are essentially an integration of the following units: coke production, water gas, producer gas, preparation and purification of the reaction mixture, conversion to ammonia, partial production of nitric acid by the Ostwald process, and final production of ammonium nitrate.

Other Fixation Processes. Other reactions can be used for the purpose of fixation. Some have been used, and others have interesting potentialities. The Serpek process is primarily designed to purify bauxite for the manufacture of aluminum.

$$Al_2O_3 + 3\ C + N_2 \rightleftharpoons 2\ AlN + 3\ CO. \qquad (a)$$

$$2\ AlN + 3\ H_2O \rightleftharpoons Al_2O_3 + 2\ NH_3. \qquad (b)$$

Reaction (a) is an electric-furnace reaction similar in many respects to the cyanamid reaction. Reaction (b) is conducted in autoclaves. Nitrogen is fixed as by-product ammonia, but in France during the First World War the process was used as a primary source of combined nitrogen.

$$Na_2CO_3 + 4\ C + N_2 \overset{Fe}{\rightleftharpoons} 2\ NaCN + 3\ CO.$$

This reaction, which has long been known (Desfosses, 1828), takes place under 1,000°C. with pure nitrogen in the presence of iron as a catalyst. The cyanide may be hydrolyzed by water under pressure to give ammonia. It attracted wide attention in the United States in 1918, where an American chemist with this in mind asserted that he could fix nitrogen in his household furnace in appreciable quantities, using little more than cast iron pipe. His point was the relative simplicity of the apparatus required, which was particularly impressive in the face of the alarming slowness of construction of the war nitrogen plants, but it was not actually used.

Many metals such as Li and Mg combine directly with nitrogen to give nitrides, from which ammonia can be obtained by hydrolysis. They have possibilities if the economic problems of producing the metals can be solved.

Extent of Nitrogen Fixation. It is difficult to convey, without actual experience, an adequate picture of the magnitude of this industry by the schematic presentations which have been used. A single plant may have a production of 1,000 tons of NH_4NO_3 a day or 300,000 tons a year. United States Nitrate Plant No. 2 (Muscle Shoals, Alabama) was designed on this scale to use the cyanamid process and represented only one-tenth of a program which never got beyond that. It was started in 1917, cost $160,000,000 to build, including the Wilson Dam completed much later, made only one trial run the week the Armistice was signed, never produced nitrate again, and has been partially used to produce phosphate fertilizer, largely experimentally. United States Nitrate Plant No. 1 was a small Haber-process plant in the same area (Sheffield, Alabama), which has similarly never been used. Germany has several large Haber-process plants, notable ones at Oppau and Merseburg, and many smaller ones with an estimated fixed nitrogen output accepted by all authorities as in excess of 1,500,000 tons a year, which is certainly greater than the rest of the world combined, and is probably potentially capable of several times that production. Japan has at least one plant located near Tokyo, built in recent years, and there are many others scattered throughout the world, including the United States, although ours tend to be individually much smaller in size.

Such plants cover hundreds of acres, and the component parts are huge industries in themselves—water purification, power, coke production, and so on. Their freight yards for the handling of raw materials rival the railroad terminals of a large city. They handle millions of cubic feet of gas mixtures a day through a maze of overhead piping which is a characteristic and impressive feature of their streets, and temporary storage facilities consisting of large gasometers in large numbers are required. In the chemical aspects of the processes, in increasing total production, the tendency is to standardize a fixed size of operating machine unit, and then multiply the number of units. One sees, therefore, many large buildings, often more than 1,000 feet in length, which are merely large covered spaces, with hundreds of identical devices lined up inside and connected with the maze of services required for operation.

The industry is nevertheless chiefly a military necessity, and in general as a source of nitric acid uneconomic as compared with Chile niter. The products, however, cover the entire field of commercial nitrogen compounds, in peace times principally so, and the demand for these is increasing enormously, with the potentiality of complete production of nitric acid and ammonium nitrate for war. Regardless of economic considerations, nitrates fixed from air are unquestionably a permanent feature of the technical landscape. Table 32 shows the trend of world production of nitrogen from the various sources in different years. World use in 1938 was about 2.7 million tons, of which about 50% was used in the United States. Production by the various processes, distributed per cent, is given in Table 33.

TABLE 32

WORLD PRODUCTION OF INORGANIC NITROGEN, DISTRIBUTION PER CENT

Year	Fixed nitrogen	By-product nitrogen	Chile niter	Total tonnage
1903	0	37	63	
1913	4	41	55	750,000
1923	42	27	31	1,200,000
1927	56	28	17	1,250,000
1935	76	14	10	2,000,000

TABLE 33

NITROGEN PRODUCTION BY VARIOUS PROCESSES OF FIXATION, DISTRIBUTION PER CENT

Process	World, 1925	Germany, 1925
Arc	7	1
Cyanamid	30	19
Haber	63	80

While all the processes are still in use, and the cyanamid process particularly not likely to be discontinued, new large plants tend to be designed for modified Haber processes. The United States, although the largest user of nitrogen compounds, has had a very slowly expanding fixed nitrogen output. It was estimated at 23,000 tons in 1927 and was probably not in excess of 250,000 tons in 1941 after some war expansion. For the war-program expansion in the United States, the theory favoring the small, scattered plant has apparently won the debate, and many new plants are standardized units with a capacity of 50 tons a day or about 15,000 tons a year, of a Haber type developed by the Du Pont organization. It will take large numbers of these to approximate German capacity.

Ammonium Nitrate, NH_4NO_3. This, from our standpoint, is one of the two principal products of the nitrogen-fixing processes. It is a white solid, which presents five polymorphic forms, two of which (the lower rhombic and the higher monoclinic) have a transition point at 32.1°C. It has a specific gravity of $1.725^{25°C.}$, melts at 169.6° C. and decomposes quietly at 210°C. according to the equation

$$NH_4NO_3 \rightleftharpoons 2\ H_2O + N_2O.$$

It is soluble 118% at 0°C. and 871% at 100°C. by weight in water.

Ammonium Nitrate as an Explosive. As an explosive, ammonium nitrate is somewhat peculiar. It does not explode by ordinary heating, nor in the range of the usual drop weight test or from ordinary blows, and is not detonated with certainty by any common size of commercial blasting cap. This remarkable lack of sensitivity prevented it from being recognized for a long time as an explosive. But many conditions, some not yet clear, render it more sensitive; and apart from the scientific facts, an accumulating series of large-scale accidents make it a material to be treated with respect as a powerful *brisant* explosive. In 1921, at the German Oppau Fixation Plant, one of the world's greatest explosions occurred. A warehouse containing some millions of pounds of the compound detonated and left only a lake some third of a mile in diameter where the plant had been. The plant was rebuilt.

There are eight possible ways in which this compound may decompose. Of these eight, three, including the one given above, are explosive.

$$2\ NH_4NO_3 \rightleftharpoons N_2 + 4\ H_2O + 2\ NO$$

$$2\ NH_4NO_3 \rightleftharpoons 2\ N_2 + 4\ H_2O + O_2$$

The last reaction, which occurs only when properly detonated is the most powerful. For it, the heat of explosion per kilogram is 384 Calories. The temperature of explosion, T_e, has been given as 2,120°; this is probably high, and the correct figure may be nearer 1,100°C. From these the other explosive constants may be computed.

Ammonium nitrate must be detonated using a large charge of T.N.T. as a primer, which in turn can be fired by a blasting cap. Tetryl and other high explosives may be used.

Ammonium nitrate is extensively used compounded with other explosives and materials, as well as alone. The commercial agricultural explosive Nitramon is substantially NH_4NO_3 and is fired with a T.N.T. primer. Mixed with T.N.T., NH_4NO_3 gives amatol, of which there are two standard compositions: 50–50 and 80–20 where the 80% component is NH_4NO_3. Originally amatol, which will be described later with T.N.T., was designed to conserve the more expensive T.N.T.; it is about as powerful. It is used in large bursting charges of all kinds, except armor-piercing shells. NH_4NO_3 is also used in some propellent explosives of the gunpowder type, for example ammonpulver. It is likewise used in dynamites, such as the old Astralit and Donarit; these are essentially mixtures of relatively small amounts of nitroglycerine with ammonium nitrate and are known also as ammonits or ammonia dynamites when they have more nitroglycerine. The nitroglycerine increases the sensitivity, and with increasing amounts improves the power. Commercial ammonia dynamites include the permissible mining explosives known as Monobels and Duobels. With powdered aluminum, ammonium nitrate yields ammonals, some of which are also permissibles. It is used in a wide variety of mixtures, including chlorate mixtures. Table 34 gives the composition of some typical NH_4NO_3 explosives.

The high in ammonium nitrate explosives compare favorably with any in the usual tests. Lead-block expansions are in the neighborhood of 300 cc., lead-block crushing around 16 millimeters, and velocity of detonation 5,000 meters per second.

Analysis. Government specifications and analysis for ammonium nitrate are as follows:[1]

---

[1] U. S. A. Specifications, 50–11–59D

Chemical requirements

	Type I, classes A and B	Type II, classes A and B
Moisture: Maximum, per cent	0.25	0.25
Ether-soluble material: Maximum, per cent	.10	.10
Water-insoluble material: Maximum, per cent	.30	1.0
Insoluble material retained on No. 40 sieve: Maximum, per cent	.01	.01
Grit	None	None
Acidity: Maximum, per cent	0.02	....
Alkalinity	None	....
Nitrites	None	None
Phenols	None	None
Ferrocyanides: Maximum, per cent	0.10	0.10
Pyridine: Maximum, per cent	.005	.005
Thiocyanates: Maximum, per cent	.01	.01
Sulphates: Maximum, per cent	.50	.50
Chlorides: Maximum, per cent	1.50	1.50
Zinc oxide: Minimum, per cent	....	.50
Zinc oxide: Maximum, per cent	None	.90
Ammonium nitrate: Minimum, per cent	97.0	96.5

Apparent density. The apparent density of type I, class B and type II, class B ammonium nitrate shall be not less than 1.15.

Granulation

	Type I, class A and type II, class A	Type I, class B and type II, class B
Through U. S. Standard sieve No. 10, minimum, per cent	....	99
Through U. S. Standard sieve No. 12, minimum, per cent	100	....
Retained on U. S. Standard sieve No. 35, per cent	....	32–48
Through U. S. Standard sieve No. 100, per cent	....	15–30

Maximum lot. 150,000 pounds.

Sampling. Take samples under such conditions that the material will absorb the least possible moisture. Select 10% of the containers but not more than 10, so as to be representative of the entire lot. From each selected container take a sample of approximately 2 pounds and break up any lumps. Mix each primary sample on a large sheet of paper by raising and lowering the diagonally opposite corners. Divide the sample into halves; place one-half in a tightly stoppered bottle and label this so that the container from which it was taken can be identified. Mix thoroughly the remaining half portions of all the primary samples. Place approximately 3 pounds of the blended material in a tightly stoppered bottle and label this so as to show the name of the material, manufacturer, plant, purchase order, date of manufacture, and number of pounds in the lot. Hold the primary samples for possible future examination should the composite sample fail to meet the requirements.

TABLE 34

AMMONIUM NITRATE EXPLOSIVES

Components	Explosives							
	Ammonals			Amatol		Ammonit	Monobels	
NH_4NO_3	72	47	93–95	50	80	79	80	70
Al	25	22	2.5–3.5					
C (charcoal)	3	1	2–3					
T.N.T.		30		50	20			
Dinitrotoluene T.N.T. Meal						17		
Nitroglycerine						4	10	10
Active base other than wood							10	
Sawdust								10
NaCl								10

Moisture. Type I. Transfer a weighed portion of approximately 10 grams of the sample to a tared weighing dish, dry at 70°C. for 5 hours, cool in a desiccator, and weigh. Calculate the loss in weight as percentage of moisture in the sample.

Moisture. Type II. In making this determination, use perchlorethylene which has been stored over anhydrous calcium chloride and a moisture tube the interior of which has been cleaned with chromic acid. Transfer a weighed 100-gram portion of the sample to the 500-cc. flask of the apparatus shown by Figure 30, and add 200 cc. of perchlorethylene. Connect a moisture tube (Figure 31) and reflux condenser by means of tight cork stoppers, and support on a ring stand with the flask resting on a wire gauze. Heat to boiling with a flame, boil briskly for 15 minutes, cool, and disconnect the apparatus. As the amount of water collected in the moisture tube usually will be too small to form 2 distinct menisci, add 1.0 cc. of distilled water from an automatic pipette, allowing it to run down the side of the tube and unite with the water collected from the sample. Read the volume of water in the moisture tube, correct for the amount added, and calculate that collected from the sample in terms of percentage of moisture in the sample.

Ether-soluble material. Transfer a weighed portion of approximately 25 grams of the sample to a Soxhlet or other suitable extractor and extract with anhydrous ethyl ether. Evaporate the ether from the extract, and dry at 100°C. to constant weight. Calculate the weight of residue as the percentage of ether-soluble material in the sample.

Water-insoluble material. Transfer the sample extracted with ether to a beaker; dissolve it in hot distilled water and filter through a tared Gooch crucible. Wash the insoluble residue in the crucible with hot distilled water until it is free from nitrate. Dry to constant weight at 100°C. Calculate the increase in weight as the percentage of water-insoluble material in the sample.

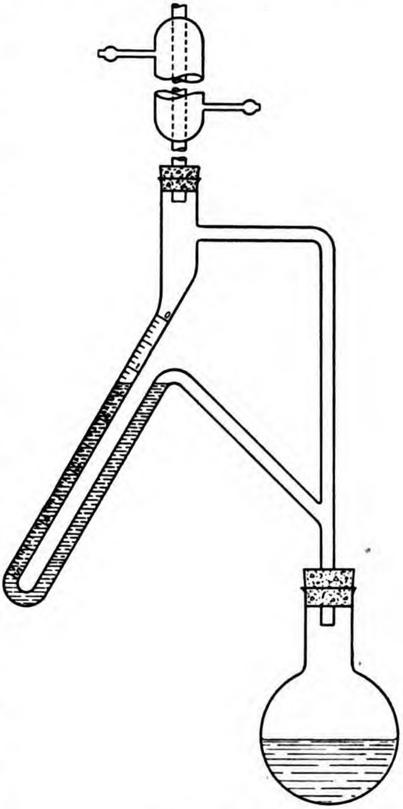


FIGURE 30

Moisture-Measuring Apparatus

Insoluble material retained on No. 40 sieve. Transfer a 100-gram portion of the sample to a beaker and dissolve in hot distilled water. Pour the solution through a No. 40 U.S. standard sieve and transfer any insoluble matter from the beaker to the sieve by means of a jet of water. Wash the insoluble matter on the sieve thoroughly by means of a jet of hot distilled water. When no more insoluble matter passes through the sieve, dry the sieve and residue remaining on it at 100°C. for 1 hour. Transfer the dry residue to a piece of paper and then to a tared glass weighing dish. Weigh the dish and paper and then from the increase in weight calculate the percentage of insoluble matter in the sample retained on the sieve.

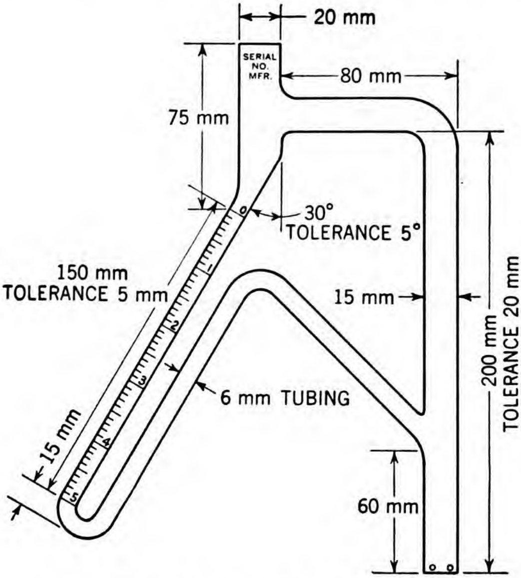


FIGURE 31: **Moisture-Collecting Tube**

Capacity—5 cc., graduated portion; *graduation interval*—as shown; *finish*—end surfaces fire polished; two diametrically placed holes near end of vapor tube as shown; *accuracy*—error not to exceed 0.05 cc. at any point.

Grit. Transfer the residue, obtained as directed in the preceding paragraph, from the weighing dish to a smooth glass slide. Rub the material on the glass by exerting pressure with a smooth steel spatula blade. Note if particles of grit are present as indicated by lack of uniformity and the persistence of a scratching noise when pressing and rubbing of the material on the glass is continued.

Acidity. Dissolve an accurately weighed portion of approximately

100 grams of sample in 400 cc. of distilled water. Filter and titrate with $N/10$ sodium hydroxide solution using methyl red as the indicator. Calculate acidity as percentage of sulphuric acid. Run a blank determination on the same amount of distilled water and methyl red and make proper correction.

Alkalinity. If the above determination shows acidity, report no alkalinity. If the solution prepared for the acidity determination is alkaline toward methyl red, titrate with $N/10$ sulphuric acid and calculate the alkalinity as percentage of sodium hydroxide. Run a blank determination on the same amount of distilled water and methyl red and make proper correction.

Nitrites. Dissolve a weighed portion of approximately 1 gram of the sample in 20 cc. of distilled water. Add 1 cc. of 10% sulphuric acid solution and 1 cc. of freshly prepared colorless 0.5% metaphenylenediamine hydrochloride solution. No yellow or yellowish-brown color should develop. If the metaphenylenediamine hydrochloride solution is colored when prepared, decolorize it by treating it with animal charcoal.

Phenols. Qualitative test. Dissolve a 50-gram portion of the sample in 75 cc. of distilled water and filter the solution. To the filtrate add 1 cc. of concentrated hydrochloric acid and 10 cc. of a saturated aqueous solution of bromine. Shake the mixture vigorously and allow to stand for at least 1 hour. Note if phenols are present as indicated by the separation of a white, crystalline precipitate.

Phenols. Quantitative determination. Dissolve a weighed portion of approximately 50 grams of the sample in 100 cc. of distilled water, acidify with sulphuric acid, and steam distill until 100 cc. of distillate has been collected. Extract the distillate with 2 successive portions of about 15 cc. of absolute ether. Treat the combined ether extracts with 5 cc. of $N/10$ sodium hydroxide solution and evaporate the ether. Add 15 cc. of distilled water to the residue, acidify with nitric acid, and add 5 to 9 drops of Millon's reagent. Boil the solution. No red coloration should develop. Prepare Millon's reagent by dissolving 10 grams of mercury in an equal weight of cold fuming nitric acid. Apply moderate heat and dilute the solution with two volumes of water.

Ferrocyanides. Qualitative test. Dissolve a weighed portion of approximately 1 gram of sample in 20 cc. of distilled water, acidify with nitric acid and warm. A blue coloration indicates ferrocyanides.

Ferrocyanides. Quantitative determination. Dissolve a weighed 100-gram portion of the sample in 100 cc. of distilled water. Add 20 cc. of normal nitric acid and warm on a steam bath for about 5 minutes. Filter into a 250-cc. volumetric flask. Wash the residue first with water and then with 100 cc. of normal sodium hydroxide solution, catching both washings in the volumetric flask. Dilute the solution with distilled water to 250 cc. Pipette 25 cc. of this solution into a Nessler tube and add 10 cc. of normal nitric acid. Add 5 cc. of a 10% ferric alum solution and sufficient distilled water to bring up to the mark. To a series of Nessler tubes add known volumes of standard potassium ferrocyanide solution (1.473 grams per liter) and the same volumes of normal potassium hydroxide, normal nitric acid, and 10% ferric alum solution as were added to the Nessler tube containing the sample. Determine the volume of sodium ferrocyanide required to give the same color as the solution tested by comparing the color of the standards with the color of the tested solution. Deduce the quantity of ferrocyanides in the sample and calculate as percentage of Prussian blue. One cc. of the standard potassium ferrocyanide solution (1.473 grams per liter) is equivalent to 0.001 gram of Prussian blue.

Pyridine. Qualitative test. Transfer a 150-gram portion of the sample to an Erlenmeyer flask and dissolve in 100 cc. of distilled water. Make the solution alkaline to litmus with 1% sodium hydroxide solution and add an excess of approximately 10 cc. Stopper the flask and warm to about 70°C. on a steam bath. Remove the stopper and examine for the odor of pyridine. If no odor of pyridine is detected, consider the pyridine content of the sample to be less than the maximum permitted. If the odor of pyridine is detected, determine quantitatively as follows:

Pyridine. Quantitative determination. Dissolve a weighed 250-gram portion of the sample in 250 cc. of distilled water in a 1-liter Kjeldahl pyrex distilling flask. Add a few drops of methyl orange solution. Connect the distilling flask to a tall, narrow gas-washing bottle, preferably a Drexel tall form with ground-in stopper. The dimensions of this washing bottle should be about 10 inches in height and 1.5 inches in diameter. Introduce about 300 cc. of sodium hypobromite solution (prepared by dissolving 100 grams of sodium hydroxide in

1,000 cc. of distilled water and then adding very slowly 30 cc. of bromine) into the wash bottle and connect with the condenser. If a Drexel wash bottle is not used, a Kjeldahl vapor trap should be introduced between the bottle and condenser. Begin distillation. During distillation add 85 cc. of $N/2$ sodium hydroxide solution, in eight approximately equal, successive portions, by means of a dropping funnel which passes through the stopper into the distilling flask. Maintain the solution in the wash bottle at a temperature of about 80°C. by means of a hot water bath. Distill over about 100 cc. into 25 cc. of $N/10$ sulphuric acid, having an adapter, connected to the condenser, dipping into the acid solution. Titrate the resulting solution with $N/10$ sodium hydroxide, using methyl orange as indicator to determine pyridine and ammonia. Add 0.5 cc. of phenolphthalein solution (1:1,000) and continue the titration until a red color results that persists for 30 seconds. This titration represents ammonia only. Run blank determinations on 25 cc. of $N/10$ sulphuric acid, using both methyl orange and phenolphthalein.

Calculations:

$$\frac{\left(\frac{AD}{B} - C\right) \times N \times 7.9}{W} = \text{percentage pyridine,}$$

where A = the number of cubic centimeters of $N/10$ NaOH required to titrate blank on 25 cc. of $N/10$ H_2SO_4 using methyl orange as indicator; B = the number of cubic centimeters of $N/10$ NaOH required to titrate blank on 25 cc. of $N/10$ H_2SO_4 using phenolphthalein as indicator; C = the number of cubic centimeters of $N/10$ NaOH required to titrate the solution consisting of distillate and 25 cc. of $N/10$ H_2SO_4 using methyl orange as indicator; D = the number of cubic centimeters of $N/10$ NaOH required to titrate the solution consisting of distillate and 25 cc. of $N/10$ H_2SO_4 using phenolphthalein as indicator; N = the normality of $N/10$ NaOH calculated from titration of 25 cc. of $N/10$ H_2SO_4 using methyl orange as indicator; W = weight of sample in grams.

Thiocyanates. Dissolved a weighed 100-gram portion of the sample in 100 cc. of distilled water, filter and dilute the solution to 200 cc. in a volumetric flask. To 20 cc. of this solution in a Nessler tube add 5 cc. of 10% hydrochloric acid, and 1 cc. of 20% ferric alum solution.

Dilute to the mark with distilled water. Compare the color with known volumes of 0.1% ammonium thiocyanate solution, treated in exactly the same way as the solution being tested, until the color is matched. Calculate the quantity of ammonium thiocyanate and express as percentage in the sample. If the presence of ferrocyanides causes difficulty in matching colors, use the following alternative method: To 20 cc. of the above solution add 1 cc. of a 1% ferrous sulphate solution, 1 cc. of a 1% ferric alum solution, 2 cc. of a 2% aluminum sulphate solution, and 2 drops of 10% ammonium hydroxide in the order named. Warm the mixture to 80°C. and filter. Wash the precipitate with 10 cc. of hot distilled water, catching filtrate and washings in a Nessler tube. Complete the determination colorimetrically as described above.

Sulphates. Dissolve a weighed portion of approximately 10 grams of the sample in a porcelain dish in 20 cc. of distilled water. Add a little more sodium carbonate (free from sulphates) than is necessary to decompose the ammonium nitrate present. Evaporate to dryness and acidify the residue with hydrochloric acid, taking precautions to avoid loss during effervescence. Evaporate to dryness. Moisten the residue with hydrochloric acid and again evaporate to dryness to insure complete removal of nitrates. Dissolve the residue in water, filter if necessary, heat to boiling, and add 5 cc. of a 10% barium chloride solution. Allow the precipitate to settle; catch this on a tared Gooch crucible and wash with hot distilled water. Dry the crucible and precipitate at 100°C. for 2 hours, cool in a desiccator, and weigh. Calculate the weight of barium sulphate and from it the percentage of ammonium sulphate in the sample.

Chlorides. Treat an accurately weighed portion of approximately 10 grams of the sample in a porcelain casserole with 80 cc. of 10% sodium hydroxide solution. Boil until all ammonia is driven off. Add 150 cc. of cold distilled water. Neutralize with nitric acid. Add a slight excess of calcium carbonate (free from chlorides) and titrate with $N/10$ silver nitrate solution, using potassium chromate as the indicator. Calculate the amount of chlorides found and from this figure compute the percentage of ammonium chloride in the sample. Run a blank and correct for chlorides found in reagents used.

Zinc oxide. Transfer a portion of approximately 10 grams of the sample to a tared 100-cc. evaporating dish and weigh. Heat on hot plate until all ammonium nitrate has been driven off; heat over a gas flame to a dull red heat, cool in a desiccator, and weigh. Calculate the weight of residue to percentage of zinc oxide. If the residue is red in color, determine the percentage of iron oxide present by dissolving the residue in hydrochloric acid, precipitating any iron present by the addition of ammonium hydroxide, catching the precipitate on a filter, igniting, and weighing. Correct the weight of residue by subtracting from it any iron oxide found present.

Ammonium nitrate. Dissolve an accurately weighed portion of approximately 1 gram of sample in an Erlenmeyer flask with 100 cc. of distilled water. Add 25 cc. of a 20% formaldehyde solution, which has been neutralized with $N/10$ sodium hydroxide solution, using phenolphthalein as the indicator. Warm the flask and contents to 60°C. and after cooling, titrate with $N/10$ sodium hydroxide solution, using phenolphthalein as the indicator.

Calculations:

$$\%\ \mathrm{NH_4NO_3} = \frac{(A \times B \times 8.005)}{C} - (D \times 1.4936 + E \times 1.2116),$$

where A = the number of cubic centimeters of NaOH used in the titration; B = normality of NaOH solution determined by standardization against ammonium nitrate of known purity; C = weight of sample used (calculated on dry basis); D = per cent of NH_4Cl in sample (see above); E = per cent of $(NH_4)_2SO_4$ in sample (see above).

Ammonium nitrate. Alternative method. Calculate ammonium nitrate from a nitrogen determination of the sample by the Du Pont nitrometer. No corrections for ammonium chloride or ammonium sulphate are necessary in this determination. For testing type II ammonium nitrate, use this method.

Apparent density. With the nitrate to be tested, fill a 300-cc. aluminum cylindrical container having an inner diameter of $2\frac{3}{8}$ inches, an inner depth of $4\frac{3}{16}$ inches with wall thickness of $\frac{1}{8}$ inch, and bottom thickness of $\frac{1}{4}$ inch. Level this off with a spatula. Cover the container by means of a No. 13 rubber stopper placed upside down over the container. Hold the stopper firmly down with the thumbs. Jolt the container 30 times against a wood block covered with a $\frac{1}{4}$-inch rubber. Fill up the void set up with more ammonium nitrate. Repeat this procedure twice, after which the container is again leveled off with nitrate and weighed. Divide the weight of the nitrate by the capacity of the cylinder (300 cc.) to give the apparent density.

Granulation. Place an accurately weighed portion of approximately 100 grams of the sample and a silver quarter, or similar object, on the specified sieve and shake vigorously for 3 minutes. Lumps or aggregates may be broken up by gentle brushing with a camel's-hair brush.

Packing. Ammonium nitrate is packed either in moisture-proof metal containers or in moisture-proof burlap-covered paper bags of a type previously approved by the Chief of Ordnance. Metal containers of the single-trip type are constructed of 22-gauge metal (U.S. Standard) and have a capacity of approximately 100 pounds. The metal containers are lined with paper of sufficient rigidity to prevent the ammonium nitrate from entering the annular grooves of the containers. The moisture-proof burlap-covered bags have a capacity of approximately 100 pounds.

Discussion Questions and Exercises

1. Write equations illustrating the oxidizing properties of nitric acid.

2. Write equations for or describe the tests for nitric acid on page 179.

3. What materials can be used for nitric-acid containers?

4. Find out the cost of nitric acid in commercial quantities.

5. How does iodine occur in Chile niter?

6. What are some of the uses of niter cake?

7. Amplify the considerations which spurred the development of the "fixed nitrogen" industry and explain why Germany's leadership in it was consistent with her military ambitions.

8. Discuss the reaction $N_2 + O_2 \rightleftharpoons 2NO$ from the standpoint of chemical equilibrium. Calculate K_p from the data on page 182, calculate Nernst's constant, and verify the statement about the effect of the arc on page 182.

9. Describe the large-scale production of liquid air.

10. Try to learn some of the anecdotes related to the discovery of the Ostwald process.

11. Calculate K_p for several temperatures for the Haber reaction and check the statements of yield in the text, for efficiency.

12. Prepare from memory a complete flow sheet of the Badische Haber process.

13. Report on the history of the Muscle Shoals enterprise, now known as the Tennessee Valley development.

14. Complete the calculations of the table of properties of explosives, in the Appendix, for NH_4NO_3.

15. Make an outline of the NH_4NO_3 analysis.

CHAPTER 11

Smokeless Powder

General Considerations. Some comment on the early history of nitrocotton as a propellent explosive has been given. After much investigation, as smokeless powder it is today the outstanding propellant and practically the only one used except for special purposes. The term smokeless powder is altogether a misnomer because, as has been seen, it is never a powder, and it does give a light yellow smoke which photographs black. Apart from the theoretic problems related to any propellant and the specific ones already discussed, the two principal difficulties in the early adaptation of nitrocellulose to this use revolved about (1) "taming" a high explosive, that is, reducing the velocity of explosion so that a weight required to propel a projectile would not shatter a gun, and (2) increasing the density so that a given weight would pack into a reasonable space. The first is solved, in part, by igniting instead of firing with a detonator. But a large quantity burning in a confined space will usually detonate of itself. The solution of the second difficulty really solved both. Vieille first colloided or gelatinized nitrocellulose with alcohol and ether and thus reduced the burning rate below 10 meters per second at ordinary pressures. Nobel accomplished the same object by colloiding nitrocellulose with nitroglycerine, producing ballistite. Cordite is essentially ballistite with a smaller proportion of nitroglycerine, so that the colloiding must be done with another solvent; with high-nitrogen cellulose this solvent is acetone, and vaseline is added. Both procedures raise the density to around 1.6. The resulting material is a true colloidal gel, a state of aggregation which is also produced by some of the materials which may be added, as polynitro derivatives. This consideration sometimes determines the choice of such addenda.

These are still the two principal types of powders—single-base or straight nitrocellulose powders, and double-base powders, which contain nitroglycerine. The double-base powders have a higher explosive potential, but some authorities assert that they foul and corrode the gun barrel too rapidly and badly. There are differences of opinion as to this. Single-base powders are standard for United States military use, and double-base powders are used only for small arms, chiefly pistols, but also for certain high velocity applications. Double-base powders are used abroad for general military purposes, and at home for sporting use. They are, nevertheless, currently acquiring increasing importance for low-caliber high-velocity projectiles of many kinds.

Many additions are made to smokeless powders, however. Materials may be added to reduce the explosion temperature such as dinitrotoluene, powdered metal, or metallic salts with other materials, and these mixtures are known as flashless powders. Grain size and shape and burning characteristics also influence flash. A flashless powder is defined as one which gives no visible flash by day, and only a dull red glow at night. Hygroscopicity can be reduced by graphite glazing and also by special surfacing processes. Powders thus treated are said to be nonhygroscopic. Powders may, then, be classified as flashless, flashless nonhygroscopic (FNH), or simply nonhygroscopic (NH). The same powder, however, may be flashless in one gun and not in another. There are other types of powder. To improve the keeping qualities, as already described, a preservative (usually diphenylamine) is added.

TABLE 35

COMPOSITION OF TYPICAL POWDERS

Powder	Straight Nitro-cellulose	Single base FNH	Double base FNH	E.C. Powder	Small arms
Nitrocellulose 12.6% N	96.0–96.5	74	49	80.4	√
Diphenylamine	.5– 1.0	1	1	0.6	√
Volatiles	3.0	√	√	√	√
Nitrocellulose 13.25% N		20			
Dinitrotoluene		5			
Nitroglycerine			20		√
T.N.T.			20		√
Hydrocellulose			10		√
$Ba(NO_3)_2$				8.0	
KNO_3				8.0	
Starch				3.0	
Metal powder					√
Graphite	√	√	√	√	√

The composition of some typical powders is given in Table 35. Where the formula does not include volatiles, it represents merely the manufacturing proportions, as all finished powders retain some of the solvent used in manufacture, and it is desirable that they should. Otherwise the powder would crumble too easily, would have a poor compression test, and would have bad or dangerous ballistic properties. Most powders also contain some graphite, used for glazing.

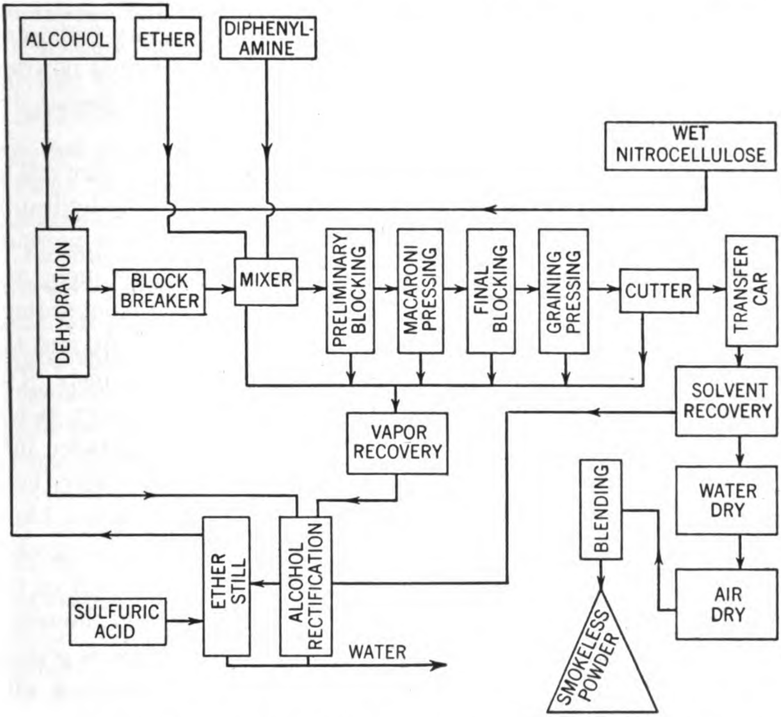


FIGURE 32: **Flow Sheet for the Manufacture of Smokeless Powder**

Manufacture. The manufacture of smokeless powder [1] begins with pyrocellulose and comprises the following principal steps:

A. Mixing with ether-alcohol or other solvent and pressing to form a colloid. Additions, if any, are made here.

B. Granulation by pressing the colloid through steel dies.

C. Treating the powder thus obtained for solvent recovery, drying, and blending.

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[1] U. S. A., TM 9-2900, *Military Explosives.*

Production of the Smokeless Powder Colloid. The pyrocotton from the wringers (see page 72), containing approximately 28% moisture, is transferred to storage and placed in warehouses to prevent freezing in winter until it is required for dehydration. The objection of *dehydration* is to remove all water from the pyrocotton and to add in its place the quantity of alcohol necessary to form the colloid with the ether that is to be added later. This amount varies within relatively small limits and is dependent upon the solubility of the pyrocotton being used as ascertained by laboratory tests, and also to a certain extent upon size of granulation of the final powder. It is customary to add $1\frac{1}{4}$ pounds of alcohol for every pound dry weight of pyrocotton.

The dehydrating operation is conducted somewhat as follows: The press consists of a cylinder and movable piston operated by hydraulic pressure. The press is charged with pyrocotton and low pressure (about 250 pounds per square inch) is applied for a few moments, thus squeezing out a portion of the excess water. The predetermined amount of alcohol is then forced into the press by a pump, and the pressure is increased to about 3,500 pounds per square inch. The alcohol functions first as an agent for displacing the water in the block and finally as a dehydrating agent. Its initial entrance into the block forces out a small portion of the remaining water; later however, it combines with the residual water and produces a block of pyrocotton nearly free of water. The first portion of this alcohol contains relatively large amounts of water and is forced out of the press into the spent-alcohol tank. The remaining amount, however, is about 90% alcohol. The spent alcohol resulting from this process is pumped back into the storage tank and eventually rectified with addition of caustic soda to decompose dissolved or suspended nitrocellulose. It is then used again either in the dehydrating process or in the manufacture of ether.

The amount of *solvent* (ether-alcohol) necessary to form the colloid is determined from previous experience of manufacture. The general practice is to vary the amount of solvent according to the web thickness of the powder; thus approximately 105% solvent is used in the manufacture of .30-caliber powder, 100% solvent for cannon powder whose web thickness is approximately 0.025 inch, and about 85% for powder having a web thickness of 0.185 inch. In the event that 100%

of solvent is to be used, or 1 pound of solvent (1 part alcohol to 2 parts ether) for every pound of pyrocotton, it is necessary that the usual dehydrating-press charge of 25 pounds dry weight of pyrocotton should produce a block weighing 33 pounds 4 ounces (25 pounds pyrocotton and 8 pounds 4 ounces alcohol).

The dehydrated blocks must be first thoroughly broken up before the next operation of mixing is commenced. For this purpose they are transferred into a rotating drum or block breaker equipped on the inside with a wire screen and iron prongs. This barrel, upon revolving, throws the block against the prongs, thus breaking it into small lumps that lend themselves more readily to the mixing operation and insure a more even colloid.

From this point, up to the time the powder is put into the solvent recovery (page 215), the product is kept in closed containers as much as possible between the various steps in the manufacturing process in order to prevent excessive losses in solvent; this is an important point not only from the economical but also from the manufacturing standpoint, since excessive loss of solvent would entail difficulty or irregularity in subsequent screening and graining operations.

The *mixing* operation is the next step in the formation of the colloid. As has been pointed out above, unless care is exercised during the dehydrating process in producing a block of uniform dehydration, it will be impossible to secure a good colloid. It is no less important that the ether be added to the mass in such a manner that the evaporation losses are minimized by incorporating the ether throughout the mass as quickly as possible. To accomplish this a mixing machine is used. It consists of a covered water-cooled tank in which two shafts bearing curved agitator blades rotate in opposite directions, giving a kneading motion to the material in the mixer. During this agitation the ether is poured in rapidly in order to minimize loss of solvent by evaporation.

It is also at this stage of the process that the so-called stabilizer is incorporated into the colloid. The material used for this purpose is diphenylamine, enough of this substance is dissolved in the ether so that the finished powder will contain between 0.90 and 1.10% (see Table 35) diphenylamine. The object of adding diphenylamine at this stage is to incorporate it thoroughly throughout the colloid so that on long-continued storage any nitrous fumes which may be liberated within the powder will be absorbed by this so-called stabilizer.

The description up to this point covers the manufacturing of straight nitrocellulose powder. If there are other addenda, they are added at this point. Some may be dissolved in the ether with the diphenylamine, if the amount and solubility permit. Or they may be made up as a dope, and added. The following processes ensure good incorporation.

The colloid is next subjected in sequence to action of a preliminary blocking press, a macaroni press, and a final blocking press. Incorporation of ingredients as accomplished in mixing is really but a preparatory stage for final formation of colloid, this last step being completed by action of the presses.

The *preliminary blocking press* consists merely of a cylinder and piston similar in action to the dehydrating press. It forms the colloid into a dense cylindrical mass by subjecting it to a compression of approximately 3,500 pounds per square inch. This so-called preliminary block is then transferred to the *macaroni press.* The operation here consists in straining the solid block of colloided matter through a heavy brass perforated plate on which are placed one 12-mesh steel plate, two sheets of 24-mesh and one sheet of 36-mesh steel wire screens, at a pressure of 3,000 to 3,500 pounds per square inch, in such a manner that the material as it is ejected is similar in appearance and size to macaroni. As it leaves this press it falls by gravity into the cylinder of the final blocking press. This is similar in every respect to the preliminary blocking press and forms the colloid into final shape before it is taken to the graining press. The block is here subjected again to heavy pressure (approximately 3,500 pounds per square inch) for 1 to 2 minutes, thus completing the colloiding of the pyrocotton. The colloid now is entirely different in appearance from the material as drawn from the mixers for it has been changed from a mass resembling light brown sugar to a dense, elastic, translucent brown or amber substance. These operations of pressing insure to the greatest possible degree a uniformly thorough action of the solvent upon the pyro, and very nearly eliminate the possibility of having uncolloided nitrocotton in the finished powder.

Graining and Cutting. The final operation of granulation of the powder occurs in the *graining-press room.* Graining presses may be set either horizontally or vertically. Their action is to force the colloid through a steel die (see page 131) in such a manner that the expressed material, which takes the form of a perforated or solid strand, will be delivered at a uniform rate of speed under control of the operator at the press. The pressure which is necessary to force this colloid through the die is very great (2,500 to 3,800 pounds per square inch) and is supplied by means of a hydraulic ram. The press head may be equipped with one or more dies, depending upon the capacity of the graining presses. When small-arms powder is being grained there may be thirty-six strands issuing simultaneously from the head. However, with a large-caliber powder such as that for 16-inch guns it is customary to use but one die. The powder issues from the press head in the form of a flexible rope which is led over pulleys to a cutting machine. This cutting machine is capable of very fine adjustment and is so manipulated that the length of the grains may be closely controlled.

Factors affecting the size of grain and its relation to the type of gun for which it is designed are discussed in Chapter 7.

Solvent Recovery. The powder as it comes from the cutter has a definite granular form and contains a considerable amount of the ether-alcohol solvent which must be removed. Hence the powder is next subjected to a drying treatment for the purpose of removing the solvent from the powder grains. This drying process is of considerable importance in producing a uniform finished powder, and includes recovery of a large portion of the ether-alcohol solvent remaining in the powder. For this reason the initial process in drying powder is one of solvent recovery, although recovery of the solvent is only incidental in the powder-manufacturing process.

Three types of equipment have been used successfully in recovery of solvent and initial drying of smokeless powder. In the chamber type the powder is placed in a metal-lined box provided with a water-sealed lid. The car type utilizes a solvent-recovery car as a drying chamber, the car being loaded directly from the powder cutters. In the tank type the powder is transferred from the cutter room to a large metal tank.

In all of these types the operation of removing the solvent from the powder is the same. Warm air is circulated through the powder and is then forced over cold coils. This change in temperature causes a precipitation of the solvent upon the coils. The saturated air, after passing over these cold coils and losing its surplus solvent, is reheated and then again forced through the powder in a continuous cycle, in this manner completing the closed system of air circulation. Length of treatment depends upon size of the powder; the larger grains requiring a greater length of time than the smaller ones. As the solvent is removed from the powder the grains partially collapse or shrink, and it is therefore necessary to control the rate at which the solvent is removed from the powder in order to produce a uniform finished product. Furthermore, if the solvent is removed too rapidly the surface of the powder grains becomes dry and hard, this making more difficult the removal of the solvent from the interior of the grains. The length of time necessary for powder to remain in the solvent-recovery building is governed by rules resulting from experiments and combining maximum efficiency with best results from the standpoint of drying.

Temperature and times of heating in solvent-recovery processes differ somewhat at different plants. A schedule which has been followed quite generally is outlined below.

For propellent powders having web thickness up to 0.095 inch: Raise to 30°C. and hold for 24 hours; raise to 38°C. and hold for 24 hours; raise to 45°C. and hold until total time of treatment has been 7 days.

For powder of heavier web than 0.095 inch: No heat for 48 hours; raise to 25°C. and hold for 24 hours; raise to 30°C. and hold for 24 hours; raise to 35°C. and hold for 24 hours; raise to 40°C. and hold for 24 hours; raise to 45°C. and hold until total time of drying of solvent recovery treatment has been 8 days.

It is not practicable from an economic standpoint to reduce the solvent content of the powder to the desired degree in the solvent recovery treatment; hence, the final drying is accomplished as a separate operation.

Under normal operating conditions an appreciable portion of the ether in the solvent is lost due to exposure of the powder mass to the atmosphere unless means are provided for its recovery. In the more modern powder factories equipment is installed for recovery of the solvent vapors from the air.

Drying. There are two separate types of drying operations, the first and most satisfactory, except from the standpoint of time, being the air-dry system. The second method is known as the water-dry system and has a great advantage as to time saving.

In the *air-dry treatment* the powder is transferred directly from the solvent recovery house to the dry house and placed in bulk in narrow bins. The time of drying varies with the granulation of the powder. For all granulations, however, there is a heating period of 30 days at 43°C. The temperature may then be raised to 55°C. The time required to drive off the volatile matter until the desired total volatile-solvent content has been secured varies from about 30 days for the 75-millimeter powder to 90 days or longer for 16-inch powder. In the case of powder having web thickness of more than 0.095 inch, a period of at least 2 weeks in the dry house without heating must precede any heating treatment.

From time to time the laboratory analyzes a sample of the powder to determine if the required external moisture and volatile-solvent contents have been reached. The desired external moisture content for air-dried powders varies inversely as the size of the grain from about 0.1% to 1.0%, while the total volatile content of the dried powders may vary from approximately 3.5% to 7.5%, depending upon the web thickness, the heavier-web powders having the greater solvent contents. Control of moisture and volatile content of finished powders is of great importance, since rate of burning and energy content of powder are reduced as the amount of solvent and moisture are increased.

The main difference between the air-dry process and the *water-dry process* is the difference in the surrounding medium. In the first case it is warm air and in the second warm water, but the object desired is the same in either case. Water is kept circulating throughout the powder at temperatures which vary by 10° increments from 25° to 55°C., for approximately 4 days for powders having a web thickness of approximately 0.020 inch. Later the powder is removed and air-dried for about 48 hours, this latter treatment requiring much less time to finish than when the powder has only the air-dry treatment. The external moisture content of water-dried powders may vary inversely with the size of powder from 0.9% to 1.4%.

A later development in the powder drying process is the so-called *continuous drier*. This differs from the ordinary dry-house treatment in that drying the powder is accomplished in between 4 and 5 hours, depending upon size of granulation. The powder enters the dry house from the water-dry system, is hoisted to a hopper, and then slides by gravity into a shaking screen. This screen removes foreign material and drops the powder to a bucket conveyor of the ordinary type. The powder is then hoisted to the top of the building where it is thrown into a drying chute. This chute is approximately 6 inches in thickness, 5 feet in width, and about 10 feet in length, and is equipped with baffles running crosswise in the direction of its smallest dimensions. A series of screens on the side wall provides the means for the passage of warm air through the powder; and a temperature of 50°C. is maintained by this means at the bottom of the chute. A shaking device near the floor is capable of such regulation that the rate of discharge from the drier and consequently the volatile content of the powder is controlled by the speed at which this shaker is operated and by the amount of clearance between the shaker and the bottom of the chute. In one of the largest war plants one continuous drier was capable of drying to correct moisture and volatile content 100,000 pounds of 75-millimeter powder in 24 hours.

Blending. The next step, and an important one from the standpoint of uniformity of firing, is the proper mixing or blending of a certain arbitrary amount of powder. For the larger-caliber guns it is customary to blend or mix a complete lot of 100,000 pounds of powder, but for the smaller-caliber powders, particularly for the small-arms powder, lots ranging from 15,000 to 50,000 pounds are more usual.

The blending operation consists merely in transference of powder by means of gravity from one bin to another, this transference resulting in thorough mixing of all the lot. These bins are so constructed that when full of a lot of powder the powder assumes the shape of a double cone with one apex pointed down toward the discharge pipe and the other apex pointed up toward the top of the bin. The proper construction of these bins from the standpoint of the correctness of angles at the sides of the bin is very important. If the sides of the bin are too steep, the powder will slide down toward the apex of the lower cone. If, on the other hand, the sides are built on too gradual a slope the powder will not flow freely from the bin and it would be necessary to use a raking device in order to empty the bin toward the end of the lot. It is essential, therefore, that a point midway between these two be found, a point so selected that the powder will not slide down the side of the bin, yet at the same time will insure a complete emptying and mixing of the lot. These angles have been determined, and when the principles are observed no difficulty results from lack of proper blending. After two or three cycles from one bin to the other have been completed, the powder is weighed and boxed.

Another type of blender was formerly used at Picatinny Arsenal. In the place of two bins set one upon the other as in the old type—an awkward arrangement which necessitated a building at least 100 feet high—two separate buildings were constructed about 100 feet apart. The bottom of one bin was connected with the top of the other by an endless belt. There were then two belts operated independently of each other for transference of the powder from the bottom of one bin to the top of the other. The arrangement at the bottom of each bin was such that the powder might be boxed in either building. When it was desired to empty one bin and transfer to the other for the purpose of blending, it was necessary only to put the belt in motion and open the chute. The speed of the belt was such that 100,000 pounds were hoisted in about 75 minutes, a speed not possible with the older type of blender. The powder was charged into a hopper at the base of one tower—from bags if coming from the dry house, or from boxes if the powder was being reblended—onto a conveyor belt, carried to the top of the second tower, and dropped into the bin until the entire lot had been transferred to this bin. The conveyor belt at the base of this second tower was then started, the powder carried to the top of the first tower, and thence into the bin, thus completing the cycle. The blending comprised four complete cycles.

After the blending is completed the lot of powder is boxed and stored. The powder container used for storage is merely an airtight zinc box about which is built a wooden box completely covering and protecting the metal inside. It holds from 110 to 140 pounds of smokeless powder. These boxes are tested for air leaks to insure the powder retaining the same moisture and volatile content as when withdrawn from the dry house. In recent years an all-metal box has been used for the larger-caliber powders.

FNH and NH Powders for Cannon. At the outbreak of the First

World War in 1914, the United States Army and Navy employed the same type of straight nitrocellulose powder, the manufacture of which has been described above. After the experiences in the war certain weaknesses in the standard propellent powder were recognized.

The standard nitrocellulose type of powder, if exposed to the atmosphere, is subject to change. The volatile solvent (ether-alcohol) used in manufacture is not completely removed, the powder retaining from 3% to 7.5%, depending upon size of grain. In a warm, dry atmosphere this residual solvent partially escapes and the rate of burning of the powder is increased. On the other hand, if the powder is exposed to a humid atmosphere, it absorbs moisture and the rate of burning is decreased. Thus, ballistic properties of the powder are appreciably affected by changes in atmospheric conditions to which the powder may be exposed. A recent change is a rifle powder of chemically- and faster-made, spherical grains.

Another objection to the pyro powder was the fact that when fired it produces a large, brilliant flash at the muzzle of the gun. This objection proved to be serious during the First World War, owing to the great amount of night firing, since the flash aided the enemy in locating positions of the guns.

The need was recognized for a nonvolatile, nonhygroscopic, and flashless powder which would still retain the property of being substantially smokeless. Such powder has been developed since 1918, and is designated FNH if flashless, or NH if used in weapons in which flashlessness is not attained.

The FNH type of powder has been obtained by adding to the nitrocellulose inert or partially inert materials for the purpose of cooling the products of combustion and reducing the hygroscopicity of the powder. Such a powder may be flashless in certain weapons but not flashless in others, since flashlessness is dependent not only upon composition of the powder but also upon relationship between quantity of powder used as a charge and length of bore of the weapon, weight of projectile, and the like. While it might appear possible to obtain flashlessness in any weapon by merely increasing the amount of flash-reducing agent in the powder composition, such a procedure may be impracticable either because of increased smoke produced or because of reduction in potential of the powder. While the present type of FNH powder has a lower potential than the standard pyrocellulose powder, it has sufficient potential to permit its use in all weapons without change in ballistic requirements.

The manufacture of the FNH powder can be carried out in the same equipment and plant used for manufacture of the standard pyrocellulose powder. However, details of the processes for the two types of powder differ in many respects.

Survey of Smokeless Powder. There are many United States government specifications related to smokeless powder, and as in other cases, they should always be consulted. In general, requirements fall under these headings:

A. Raw materials. Some analytical methods will be given.

B. Manufacture. This is similar to the process already given, with appropriate modification for the type of powder.

C. Sampling. To secure a representative sample for any chemical analysis is always an important problem. Maximum lots range for smokeless powder from 10,000 to 150,000 pounds, in containers. The ballistic sample, which must be large and suitable for firing tests, is selected in aliquot parts from containers selected at random, usually 10 and not fewer than 6. The chemical sample is taken from the same containers, carefully handled, put up in air-tight glass jars, labeled so that it can be completely identified, and is usually not less than 5 pounds in weight.

Grain size and shape characteristics have been described in Chapter 7. Pistol powders are usually in small flake or disk form, for which the chief requirement is that they be free from smaller particles or dust. All other powders are of the single- or multiperforated types already described.

Ballistic and weapon tests are not primarily the purpose of this volume. The principal tests employed for all types of powder are: (1) service velocity; (2) velocity uniformity; (3) pressure—minimum, average, and maximum; (4) excess charge; (5) smokelessness; (6) fouling and corrosion. The last two are chiefly for small-arms powders. Some of these tests are described in Chapter 16.

The next few sections will describe some of the chemical tests. They include tests for raw materials, and for pyrocellulose and smokeless powder, and relate specifically to a straight nitrocellulose powder. Tests, of course, in a given case must be appropriate to the type of powder.

Testing Raw Materials.[2] *Method for analysis of cellulose.* Moisture: Not less than 3 grams (preferably 5 to 6 grams) is weighed out in a ground-glass covered moisture dish of suitable size, or an aluminum dish provided with a tight-fitting cover, and dried to constant weight in an oven at 105°C. (about 1½ hours). The dish is placed in a desiccator, covered, and when cool, weighed. The loss in weight is calculated as percentage of moisture. At the same time that a sample is taken for moisture, a 2-gram sample is weighed out for the alkali-soluble determination.

Extractive matter: The dried sample from the above moisture determination is placed in a Wiley or Soxhlet extractor and sufficient redistilled ethyl ether for the extraction is added. After the sample has been extracted on the steam bath for 3 hours, the ether is transferred to a weighed beaker or evaporating dish and evaporated to dryness on a steam bath. The residue is heated for 30 minutes in an oven at 100°C., cooled in a desiccator, and weighed. From this the percentage of extractible matter based on the weight of dry cotton is calculated.

Ash: Approximately 2 grams of the sample are placed in a weighed crucible and moistened with concentrated nitric acid and digested for about 1 hour on a steam bath or hot plate, then heated gently at first over a flame or in a muffle furnace until all combustible material is consumed. The crucible is then cooled in a desiccator and weighed. From the increase in weight the percentage of ash is calculated in relation to dry weight of sample.

Alkali soluble: The 2-gram sample of the cellulose weighed out with the moisture sample is used for the alkali-soluble determination. The sample is heated in a 250-cc. Erlenmeyer flask provided with a rubber stopper through which passes a long glass tube which serves as an air reflux, with 100 cc. of caustic soda solution ($7.14\% \pm 0.1\%$) for 3 hours at 100°C. After heating is completed the cellulose and solution are poured into a beaker containing a liter of distilled water. The alkali is neutralized with a decided excess of acetic acid. The undissolved cellulose is filtered within 5 minutes on a weighed Gooch crucible having an asbestos mat, and thoroughly washed successively with hot water, alcohol, and ether. It is then dried rapidly to constant weight at 102° to 105°C. The loss is then calculated as percentage of alkali-soluble material on the basis of the dry weight of cellulose.

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[2] Various U. S. specifications.

Lime, chlorides, and sulphates: A 5- to 10-gram sample is boiled for about ½ hour with approximately 100 cc. of distilled water. The water is then filtered off, a small portion slightly acidified with hydrochloric acid, and brought to a boil. While hot, about 1 cc. of 5- to 10% barium chloride solution is added. If only a faint cloudiness is noted the sample is considered as containing but a trace of sulphates. Another small portion of the water extract is taken and acidified slightly with nitric acid. A few drops of silver nitrate solution are added. If only a slight cloudiness is noted, the cellulose may be considered as containing but a trace of chlorides. Another small portion of the water extract is made slightly acid with hydrochloric acid and then faintly ammoniacal with ammonium hydroxide. A few cubic centimeters of a saturated solution of ammonium oxalate solution is added and the solution is boiled. If but a faint cloudiness is noted without the formation of a precipitate the material may be considered as having but a trace of lime.

Hypochlorites: Approximately 1 gram of the sample is placed in a uniform layer on the bottom of a 150-cc. beaker. Ten cubic centimeters of a 10% solution of potassium iodide are poured carefully on the center of the moistened cellulose. A slight violet coloration indicates the presence of hypochlorites. The test is sensitive to about 0.01%.

Absorbency: The absorbency of the cellulose is determined by taking approximately 1 gram of the dried sample, rolling it into a ball in the palm of the hand, and placing it lightly on the surface of approximately 200 cc. of water in a 250-cc. beaker. The ball will sink below the surface of the water within 10 seconds if the sample has satisfactory absorbent properties.

Viscosity: If the viscosity of the cellulose is specified in the contract, it is determined by the method given in the *Journal of Industrial and Engineering Chemistry*, Analytical Edition (1, 49, 1929).

Method for analysis of diphenylamine. Color: A portion of the sample of diphenylamine is ground to pass a 10-mesh screen (opening, 0.065 inch). The color is determined by visual examination of the ground material and should not be darker than a light brown.

Setting point: From 80 to 100 grams of the sample are ground to pass a 10-mesh screen, after which the ground sample is dried for 4 hours at 40°C. In lieu of drying, the sample may be melted and mixed with 20 grams of anhydrous calcium chloride or sodium sulphate, and the mixture stirred for 15 minutes at a temperature of 80°C., after which the mineral salts are allowed to settle and the molten diphenylamine poured off. The dried sample is transferred to the inner tube of a solidification-point apparatus (see page 270) and melted. This tube is then placed in the apparatus and a standard thermometer is so adjusted that the bulb is in the center of the diphenylamine with a side thermometer in position for the emergent-stem correction. The molten material is vigorously stirred by means of the hand stirrer and the point at which the temperature begins to rise is carefully noted. When solidification begins, the temperature is recorded every 15 seconds until a maximum reading is obtained. The maximum temperature reading is corrected for the emergent stem by adding the value calculated from the product

$$N(T - t) \times 0.000159,$$

where N = number of degrees in exposed mercury column, t = average temperature of exposed mercury column determined by means of a second thermometer suspended so that its bulb is in the midpoint of exposed mercury column, T = uncorrected setting point, and 0.000159 = the coefficient of expansion of mercury in glass. The corrected reading is recorded as the setting point of the sample and should fall within the range of 51.7°C. to 53°C.

Solubility: Twenty-five grams of the sample are dissolved in 100 cc. of ethyl ether of a specific gravity 0.717 to 0.723 at 20°/20°C. This solution is filtered through a tared Gooch crucible and washed thoroughly with additional solvent. The crucible is then dried at a temperature of 100°C., cooled in a desiccator, and weighed. The percentage of insoluble matter is then calculated and should not exceed 0.02%.

Moisture: Three to five grams of the powdered sample are weighed in a tared weighing bottle of about 5 centimeters diameter. The weighed sample is heated for 4 hours at 40°C. or placed in a sulphuric acid desiccator at room temperature for 24 hours. The loss in weight, calculated as per cent, is recorded as the percentage of moisture and should not exceed 0.2%.

Acid or alkali: Twenty grams of the ground sample are placed in a 250-cc. Erlenmeyer flask and 50 cc. of nearly boiling distilled water is added. The flask is immediately stoppered and shaken vigorously for about 10 minutes. It is then cooled to 25°C. and the solution is filtered, retaining the diphenylamine in the flask. This extraction is repeated with 50 cc. of hot water. A few drops of phenolphthalein are added to the filtrate, after which it is titrated with $0.1N$ alkali if acid, or $0.1N$ acid if alkaline. A blank determination is made on the water and used as a correction in the titration of diphenylamine for any acidity or alkalinity found. The acidity or alkalinity is calculated to hydrochloric acid or sodium hydroxide as the case may be. The sample should not contain more than 0.005% of free and combined acid or alkali. The filtrate in this determination is reserved for the next test.

Aniline and aniline salts: The filtrate from the acid or alkali determination is used for the determination of aniline or aniline salts present. A bromide-bromate method is used for this determination. The filtrate is transferred to a glass-stoppered Erlenmeyer flask and 25 cc. of $0.1N$ bromide-bromate water solution are added by means of an accurate 25-cc. pipette. The bromide-bromate solution contains 2.784 grams of $KBrO_3$ and 15 grams of KBr per liter. The mixture is cooled to 15°C. and 5 cc. of concentrated hydrochloric acid is added. After 1 minute, 10 cc. of 10% of potassium iodide solution are added. The contents of the flask are then titrated with $0.1N$ sodium thiosulphate solution using starch as an indicator. A blank determination is made on 25 cc. of the bromide-bromate solution exactly as described above. In calculating the results, correction is made for the amount of diphenylamine dissolved in 100 cc. of water at 25°C. by subtracting 0.33 cc. from the number of cubic centimeters of normal thiosulphate solution representing the difference between the blank and sample titrations. The percentage of aniline is equal to

$$\frac{(A - B)(N - 0.33)\ (0.01551)\ (100)}{W},$$

where A = the number of cubic centimeters of $Na_2S_2O_3$ solution used in blank titration, B = the number of cubic centimeters of $Na_2S_2O_3$ solution used in sample titration, N = the normality of $Na_2S_2O_3$ solution, and W = the weight of sample taken. The amount of free aniline or aniline salts contained in the sample will not exceed 0.1%, calculated as $C_6H_5NH_2$.

Method for analysis of mixed acids. Suspended matter: A portion of approximately 40 grams of the sample, accurately weighed from an acid-weighing bottle, is filtered through a tared Gooch crucible containing a carefully prepared and dried asbestos mat. The mud or suspended material held on the asbestos mat is washed with at least five 20-cc. portions of anhydrous alcohol. The anhydrous alcohol used may be prepared by allowing 95% alcohol denatured with 0.5% of benzene to stand over anhydrous copper sulphate, and filtering the alcohol before use. The crucible is dried for 3 hours at 125°C., cooled in a desiccator, and weighed. The increase in weight of the crucible is calculated as percentage of suspended matter.

Ash: The filtrate obtained from the determination of suspended matter is placed in a tared platinum or silica dish, heated slowly with a Bunsen flame under a hood until the evolution of fumes has ceased, and then heated to a dull red for 2 or 3 minutes, cooled in a desiccator, and weighed. It is heated for a further short period to determine if constant weight has been obtained. The increase in weight of the dish is calculated as percentage of ash.

Total acidity: By means of a Lunge acid-weighing pipette, a carefully weighed portion of approximately 1.5 grams of the sample is carefully transferred to a 500-cc. Erlenmeyer flask containing about 50 cc. of distilled water. Two or three drops of phenolphthalein or methyl red indicator are added and the solution titrated with standardized $N/2$ or $N/3$ sodium hydroxide solution. The total acidity is calculated in terms of sulphuric acid after subtracting from the weight of mixed acid the weight of suspended matter and ash calculated to be present.

Total nitric acid: About 5 cc. of special nitrogen-free sulphuric acid (94.5% ± 0.5%) are placed in the cup of the generating bulb of the Du Pont nitrometer. A known weight of the sample of mixed acid, estimated to contain approximately 0.50 to 0.55 gram of nitric acid, is rapidly introduced into the cup, the acid being stirred by means of a small glass rod. As soon as the mixed acid has been added, the stopcocks of the acid pipette are closed, the cap on the pipette quickly replaced, and the acid in the cup drawn into the generating bulb. Four 5-cc. portions of the sulphuric acid are used to wash the sample thoroughly into the generating bulb, making a total consumption of 25 cc. of sulphuric acid used in the test. It is customary to reweigh the pipette with as little delay as possible after the first washing with 5 cc. of sulphuric acid to minimize any evaporation losses or absorption of moisture from the air. When the sample has been completely drawn into the generating bulb, the upper stopcock is closed, the lower stopcock allowed to remain open, and the mercury reservoir is adjusted so as to give a slightly reduced pressure in the generating bulb. The bulb is shaken gently until most of the gas has been generated. The mercury reservoir is adjusted so that the mercury in the generating bulb drops nearly to the lower shoulder and the lower stopcock is closed. The bulb is shaken vigorously for 3 minutes, then is replaced on the rack, with the lower stopcock open and the mercury reservoir adjusted until the mercury in the generating bulb is at approximately the same height as the mercury in the reservoir. This adjustment is for the purpose of bringing the pressure inside of the generating bulb to approximately one atmosphere, so that the solubility of the nitric oxide gas in the sulphuric acid will not vary too widely. The lower stopcock is closed and the bulb shaken vigorously for an additional minute. The gas is transferred to the measuring tube and the levels of the mercury in the compensating tube and measuring tube are adjusted to approximately the same height. The gas is allowed to stand for about 20 minutes in order to permit equalization of the temperature of the gas in the two tubes, the mercury levels are adjusted closely with a leveling device, and the burette is read. The percentage of total nitric acid is calculated by the formula

$$\text{total nitric acid} = \frac{4.4975A}{B},$$

where A = the reading on the gas burette of the nitrometer, and B = the weight of the sample of acid taken minus the weights of suspended matter and ash calculated to be present.

Oxides of nitrogen: A known weight of approximately 10 grams of mixed acid is transferred to a 300-cc. Erlenmeyer flask containing 75 cc. of distilled water. A standardized $0.1N$ potassium permanganate solution is added at intervals with agitation until the end point is observed, indicated by a permanent delicate pink coloration. The percentage of oxides of nitrogen is calculated as nitrogen dioxide by the formula

$$\text{oxides of nitrogen} = \frac{4.601AB}{C},$$

where A = the number of cubic centimeters of $KMnO_4$ solution used, B = the normality factor of the $KMnO_4$ solution, and C = the weight of sample taken minus the weights of suspended matter and ash calculated to be present.

Sulphuric acid: The sulphuric acid content of the mixed acid free from suspended matter and ash is calculated as follows·

$$\text{sulphuric acid} = A - 0.77816B,$$

where A = total acidity, expressed as sulphuric acid, and B = total nitric acid.

Nitric acid: The nitric acid content of the mixed acid free from suspended matter and ash is calculated as follows:

$$\text{nitric acid} = A - 1.3695B$$

where A = total nitric acid, and B = oxides of nitrogen.

Water: The water content of the mixed acid free from suspended matter and ash is calculated by subtracting from 100% the sum of the percentages of sulphuric acid, nitric acid, and oxides of nitrogen.

If it is desired, a Gooch crucible with an asbestos mat may be substituted for the filter paper if the mat is thick and compact, and the operator can check results by this method with those by the method described above.

Method for analysis of ethyl alcohol. Content: The specific gravity at 20°/4°C. is determined by means of a calibrated hydrometer or pycnometer. The percentage of alcohol by volume is obtained by reference to the tables of the *Official and Tentative Methods of Analysis* of the Association of Official Agricultural Chemists.

Acidity: Fifty cubic centimeters of neutral distilled water is placed in a 250-cc. Erlenmeyer flask and a 50-cc. portion of the sample added measured by means of a graduated cylinder. Six drops of gallein indicator (made by dissolving 1 gram of gallein in 1 liter of neutral ethyl alcohol, approximately 95% by volume) are added and titrated with approximately $N/10$ sodium hydroxide or potassium hydroxide solution. The percentage of acidity in the sample is calculated:

$$\text{percentage of acidity as acetic acid} = \frac{0.12AB}{C},$$

where A = number of cubic centimeters of hydroxide solution, B = normality of hydroxide solution, and C = specific gravity of alcohol.

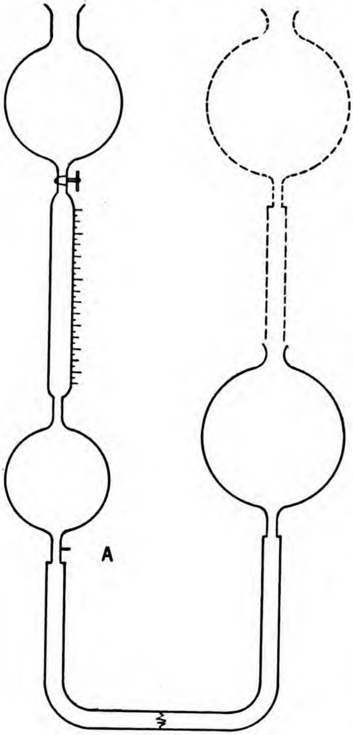
Residue: A 100-cc. portion of the sample, measured by means of a pipette, is transferred to a tared evaporating dish. The liquid is evaporated on a steam bath to dryness, then dried for 2 hours at 100°C., cooled in a desiccator, and weighed. The increase in weight of the dish is calculated as percentage of residue.

$$\text{percentage of residue} = \frac{A}{B},$$

where A = weight of residue, and B = specific gravity of sample.

Aldehyde: Silver nitrate and sodium hydroxide solutions are prepared containing 9 grams of compound per 100 cc. of distilled water. By means of a pipette, 1 cc. of the silver nitrate solution and 1 cc. of the sodium hydroxide solution are transferred to a graduated cylinder (5 to 10 cc. capacity) and approximately 1 cc. of NH_4OH (specific gravity .90), or an amount sufficient to dissolve the precipitate formed by addition of the sodium hydroxide to the silver nitrate solution is added. By means of a pipette or burette, a 10-cc. portion of the sample is transferred to a clean, glass-stoppered bottle or flask and 1 cc. of the solution from the graduated cylinder added. The bottle is shaken well and allowed to remain in a dark place for 1 hour. The solution is filtered and the clear filtrate is tested for unreduced silver by adding 1 cc. of a 10% solution of sodium chloride. If any precipitate is formed, as shown by the cloudiness of the liquid, it is indicated that the alcohol contains not more than a trace of aldehyde. When the test is completed the solutions used are destroyed, as a sensitive silver salt may be formed.

Fusel oils and the like: Both of the following tests are made. (a) By means of a graduated cylinder, a 10-cc. portion of the sample is transferred to a clean, clear test tube. One cubic centimeter of a solution made by dissolving 1 gram of potassium permanganate in 1 liter of distilled water is added. If the color of the mixture turns yellow in 20 minutes, fusel oil or other organic impurities are indicated to be present. (b) By means of a graduated cylinder, a 10-cc. portion of the sample is transferred to a clean, clear test tube. Ten cubic centimeters of chemically pure sulphuric acid (specific gravity 1.84) is added. If a yellow color results, the presence of organic impurities is indicated.



Benzenometer

Benzene: By means of a graduated cylinder, a 100-cc. portion of the sample and 200 cc. of distilled water are transferred to a 1 liter side-neck distillation flask fitted with a straight glass condenser having a water jacket approximately 40 centimeters long, 35 millimeters in diameter, and a 10-millimeter central tube. The mixture is distilled at a rate of 1.0 to 1.5 cc. per minute and 20 cc. ± 0.10 cc. is collected in a suitable graduated container. If it is thought because of a cloudy appearance of the mixture after dilution with the water that the benzene content exceeds 0.75%, an additional 10 cc. of the distillate is collected in a separate container. The first 20 cc. of the distillate collected is transferred to the receiving bulb of the benzenometer (see illustration). To this distillate 15.0 ± 0.10 cc. of a 2.5% to 3.0% solution of potassium dichromate and 3.0 ± 0.1 cc. of hydrochloric acid (specific gravity 1.20) are added from a burette. The bulb is closed with a well-fitting straight-sided rubber stopper, shaken for 2 to 3 minutes, and allowed to stand for 15 minutes or until an olive-green color develops, indicating complete oxidation of the alcohol to acetic acid. It is important that the oxidation be complete, otherwise values that are too high may be obtained. The solution is carefully drawn into the graduated tube and lower bulb by slowly lowering the mercury reservoir. After about 15 minutes, when the drainage of the liquid from the walls of the receiving bulb is complete, the exact volume of the liquid is read; it is approximately 37 cc. The volume of the tube and the lower bulb from the mark on the bottom of the lower bulb to the zero mark on the tube is 37.5 cc. If the volume of the liquid is not within 0.5 cc. of the zero mark, sufficient dichromate solution is added to increase the volume to 37.0 cc. The mercury reservoir is slowly raised until all of the solution has been transferred to the receiving bulb and 10 cc. of petroleum ether is added. The rubber stopper is inserted in the mouth of the receiving bulb and shaken thoroughly for 2 or 3 minutes. The mercury reservoir is slowly lowered until the mercury is level with the point marked A below the lower bulb in the illustration. It is allowed to stand for at least ½ hour in order to effect complete separation of two layers of aqueous solution and petroleum ether, and the decrease in volume of the aqueous solution caused by the extraction of the benzene by the petroleum ether is noted. If the 10-cc. additional distillate is collected, it is treated in exactly the same manner as the 20-cc. portion, and the values obtained are added. A blank determination is made on the same amount of absolute alcohol as of distillate used (20 or 30 cc.) and a correction made, if any is found.

Method for analysis of ether. Color: Visual comparison is made of the ether and water in test-tubes of 25 cc. capacity.

Nonvolatile residues. One hundred cubic centimeters of the sample is transferred to a tared beaker or evaporating dish, evaporated to dryness on a steam bath, and dried at 100°C. for 1 hour. This dish is cooled in a desiccator and weighed. The gain in weight is calculated as percentage of nonvolatile residue as follows:

$$\text{per cent of nonvolatile residue} = \frac{\text{weight residue}}{\text{specific gravity}} \times 100.$$

The specific gravity is determined by means of a standardized hydrometer, Westphal balance, or a specific-gravity bottle, and expressed as specific gravity at 20/20°C.

Acidity: Fifty cubic centimeters of alcohol are placed in an Erlenmeyer flask, five drops of phenolphthalein added, and neutralized with approximately $0.1N$ NaOH. One hundred cubic centimeters of the ether is added, mixed, and titrated with the standard alkali to a faint pink.

The Du Pont Nitrometer. The determination of nitrogen is important in most explosives, and for pyrocellulose, smokeless powder, nitrate explosives in general, and a few nitro explosives, can be done by means of the nitrometer. Other methods are given in Chapter 16. The nitrometer is based upon the principle that certain compounds, upon intimate contact with sulphuric acid in the presence of mercury, yield their nitrogen entirely as gaseous nitric oxide (NO). By measuring the volume of nitric oxide obtained the percentage of nitrogen in a known weight of sample can be computed.

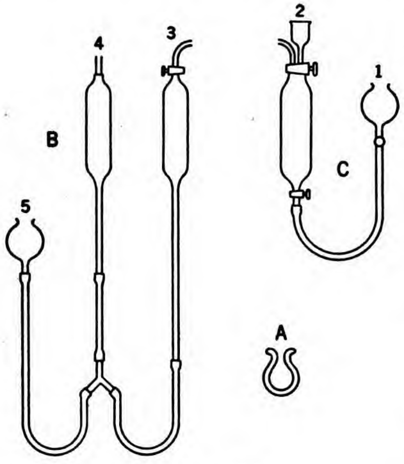


FIGURE 33
The Du Pont Nitrometer

The Du Pont nitrometer, which is a modification of the Lunge and others, avoids the necessary correction of the volume of nitric oxide for barometric pressure and temperature. The principle is to enclose in the system a volume of air such that under some conditions it occupies a marked volume, which volume is that which it would occupy at 20°C. and 760 millimeters pressure. By subjecting the nitric oxide and the air simultaneously to the same conditions by adjustment of the apparatus, and at the same time making the air conform to the marked volume, the volume of the nitric oxide becomes that which it would occupy at 20°C. and 760 millimeters. The volume of nitric oxide may then be read directly from the tube containing it, in per cent of nitrogen, if that tube is properly calibrated for 1 gram of sample, which is the usual weight (see Figure 33).

The apparatus consists essentially of the two parts *B* and *C*, which are made of glass and rubber connector tubing, and are properly supported in a position about as shown by a stand with movable clamps to permit the adjustment of the various levels which will be described. The stand must be reasonably strongly constructed, as the apparatus when filled holds about 50 pounds of mercury. *A* is merely a glass

U-tube, which may be made of ordinary tubing, with the arms about 3 inches long. Explosions sometimes occur in using the nitrometer, and the operator should always wear a mask of a standard type during actual determination.

Setting up and calibration of the air compensator. On first setting up, the tip of the tube at 4 is open (it is sealed later) and should be about 2 inches long. Place B and C in the stand about in the relative positions shown. Put a quantity of mercury into 5 such that with stopcock 3 open, it fills 3 and 4 while there is still some in 5. Put a quantity of mercury in 1 such that with stopcocks on 2 open and mercury just in the upper cup of 2 there is still some in 1.

Close the side arm of 2 with a piece of short rubber tubing and pinch clamp. With the upper stopcock of 2 closed and the lower open, fill the side-arm with mercury up to the pinch clamp by raising 1. Then similarly open the upper stopcock and fill 2 with mercury until there is a little in the cup, and close the stopcock. Place 25 cc. of 94–95% H_2SO_4 in the cup, open the upper stopcock, and by lowering 1, draw in the acid and air until the lower level of acid is just above the lower stopcock. Close the upper stopcock. Shake the bulb vigorously to dry the air, and repeat three times at intervals of 15 minutes.

Fit a piece of rubber connector tubing to 4, and with stopcock 3 closed, raise 5 until mercury fills the tubing to the tip. Try not to lose any. Connect the tubing to the side arm of 2 (which is full of mercury). Run the dry air into 4 by raising 1 until, with the stopcock of 3 now open, and the mercury in 3, 4, and 5 on the same level, the reading in 3 is about 12.50. Sighting and adjusting these levels requires practice and care. A rectangular block with mirrors on two contiguous faces, so mounted that the levels can be brought close together by reflection, is a useful device. Now seal off the glass outlet tube of 4 with a small blowpipe flame.

Dry another portion of air in 2 using the procedure as before. Fit a piece of rubber connector tubing to 3 and with the stopcock 3 open, by raising 5 fill to the tip, without loss, with mercury and attach to the side arm of 2 which is again full of mercury. Transfer air to 3 until with mercury in 3, 4, and 5 on the same level, the reading in 3 is about 12.50. These levels do not have to be either exact or equal. Fill the small manometer *A* with concentrated H_2SO_4 so that it is just above the middle of the side arms. Close stopcock 3 quickly, disconnect 2 from 3 at 3, and replace it by the manometer using a short stiff piece of rubber tubing which will support it, and open stopcock 3. Allow the apparatus to stand for 30 minutes to reach constant temperature.

Adjust the mercury in 3, 4, and 5, so that the air in 3 is under atmospheric pressure as shown by the acid in A. Close stopcock 3. Read carefully the level on graduated scale 3, and record also the temperature and pressure, V', T', P'. Calculate the volume of air, V, in 3 at 20°C., and 760 millimeters pressure as follows:

$$V = V' \frac{P' \times 293 \times (1 - 0.00018t')}{760 \times (273 + T')(1 - 0.00018 \times 20)}$$

The factor $(1 - 0.00018t')$ represents the correction for the coefficient of expansion of mercury in the barometer, at t', the temperature of the barometer. Adjust the levels of mercury in 3, 4 and 5 so that with levels 3 and 4 the same, the level in 3 reads V exactly. The height of mercury in 4 is then marked by a strip of paper pasted on the tube. This is the standard volume with which every volume of nitric oxide is to be compared. Once this operation is done, the nitrometer may be used until 4 is opened, or by some error air is lost from 4. Stopcock 3 may now be opened, the air in 3 discarded, and C may be stripped of acid, cleaned, and dried (but the mercury left in).

Standardization with chemically pure KNO_3. The scale readings of 3 should now be calibrated. A sample of chemically pure KNO_3 is recrystallized three times from 95% alcohol, finely ground, and dried for 3 hours at 135° to 150°C., or constant weight. For standard operation, room temperature must be between 15° and 32°C. C must be freed of any nitrogenous impurities from previous determinations.

The outlet tube of C is closed with connector tubing and a pinch clamp and filled with mercury to the clamp. Then 2 is filled with mercury up to the stopcock but *not* into the cup. Exactly 1 gram of KNO_3 is weighed out in a small weighing bottle. Then 20 cc. of sulphuric acid 94.5 ± 0.5% are measured into a graduated cylinder, 10 cc. run into the cup 2, and the KNO_3 dissolved in the acid in the cup. A portion of the balance may be used to wash the KNO_3 from the weighing bottle in small rinsings. This procedure may be more useful in other cases. The acid and KNO_3 mixture is then drawn into the nitrometer (***Caution!*** Admit no air!) and the cup washed with at least two further rinsings, which are likewise drawn in with care. The total volume is 20 cc. This is the point where explosion may occur in other cases.

With the lower stopcock of the generating bulb open and the mercury bulb low enough to give a reduced pressure in 2, the generating bulb is gently shaken until the larger portion of gas has been generated. The generating bulb is then raised until the mercury drops nearly to the lower shoulder, the lower stopcock closed, and the bulb is shaken vigorously for 3 minutes. Replace on the rack, open the lower stopcock, and allow to stand for 10 minutes. Close the lower stopcock, and repeat the shaking for 3 minutes, adjusting the mercury as before.

Now connect the side arms of 2 with 3 by connector tubing, making sure that there is an unbroken column of mercury filling 3 and extending to contact with the NO. Transfer the nitric oxide to 3. (By manipulation, as it is nearly run over, the sulphuric acid can be gotten into the cup, so that no acid goes into 3.) Then close stopcock 3. The positions of 3, 4, and 5 are adjusted until the level of mercury in 3 and 4 is about the same. The apparatus is allowed to stand 20 minutes. The mercury levels of 3 and 4 are then carefully and exactly equalized with a leveling device, and the reading in 3 is taken. It should be 13.85, and is to be used as a calibration.

The standardization is essentially a determination and the procedure is the same, except that other materials may be more difficult to handle than KNO_3. The nitrometer may also be standardized with a nitrocellulose blend which has been analyzed with a standard nitrometer.

Testing Nitrocellulose. *Solubility in ether-alcohol.* The official temperature for this determination is 15.5°C., and in any case where the material does not comply with the specification or where greater accuracy is desired, the complete determination is made at this temperature, the solvents being brought to this temperature before their addition to the sample. Nitrocellulose is more soluble at 15.5°C. than at a higher temperature. Ether and alcohol used should be of the quality prescribed for use in manufacture of smokeless powder.

Volumetric method: One gram of the dry sample is placed in an

Erlenmeyer flask and 75 cc. of alcohol is added; the mixture is shaken thoroughly for about five minutes and allowed to stand for two hours. Then 150 cc. of ether is added and the mixture thoroughly shaken and allowed to stand stoppered overnight. It is desirable to start this determination early in the day in order to give it plenty of agitation before standing overnight, as agitation facilitates solution.

The process used in the remainder of the determination depends upon the grade of nitrocellulose being tested, on account of the variation in the solubility of the different grades.

In the case of pyrocellulose, the mixture in the flask is thoroughly shaken the next morning and transferred to a special solubility tube of the following dimensions: total length, 21 inches; inside diameter, 1.35 inches; the lower end constricted for a length of 2 inches to an inside diameter of 0.3 inch and graduated in 0.1 cc. The constricted portion should be tapered gradually from the large part of the tube. After standing in the solubility tube until the insoluble material has settled completely as indicated by the volume of this material remaining constant over a period of one hour, the volume occupied by the insoluble and semisoluble matter is read in cubic centimeters from the scale on the tube. If the reading is 0.25 cc. or less, the percentage of insoluble matter is considered to be 1% or less. Should the reading exceed 0.25 cc. the gravimetric method will be used as follows:

Gravimetric method: The clear liquid in the solubility tube obtained as above is siphoned off to about $\frac{1}{4}$ inch from the upper surface of the settled residue. Then alcohol is added to one-third the capacity of the tube and shaken vigorously; next, ether is added to a level about 3 inches from the top, and again the tube is shaken and the contents allowed to settle. This process of washing by decantation is repeated four times, and after the fourth decantation the insoluble residue is completely washed into a beaker with a small quantity of ether-alcohol solution. The contents of the beaker are filtered through a weighed Gooch crucible with an ignited asbestos mat, washed free from soluble nitrocellulose with ether-alcohol solution, dried at a low temperature until no odor of ether can be detected and then at 100°C. to constant weight, cooled, and weighed. The crucible is then carefully ignited over a free flame, cooled, and weighed again.

The loss of weight on ignition is considered as the insoluble nitrocellulose.

In the case of guncotton or blends of pyrocellulose and guncotton, 100 cc. of the clear solution is drawn from the solubility tube (without disturbing the settled layer of insoluble material) and run into an aluminum can 50 millimeters in height by 90 millimeters in diameter, with tightly fitting cover, which has previously been dried and weighed. The soluble nitrocellulose is now precipitated from the clear solution in the can by the addition of distilled water. A finely divided precipitate of fibrous appearance is desired, and is best obtained by first heating the solution on a steam hot plate (the tared aluminum can should not come in contact with steam or hot water) to evaporate part of the ether, then adding about 50 cc. of distilled water gradually with continued heating and stirring. The exact procedure for obtaining the best results must be determined by experience. After the nitrocellulose has been precipitated, heating is continued until the liquid is evaporated just to dryness. The can with contents is then dried in an oven at 95° to 100°C for $1\frac{1}{2}$ hours, cooled in a desiccator, and weighed. A check weight should be obtained after additional drying for $\frac{1}{2}$ hour. The increase in weight of the can is the weight of soluble nitrocellulose. The percentage of the latter is calculated as follows:

$$\text{per cent of soluble nitrocellulose} = \frac{A}{B} \times 100,$$

where A = the weight of soluble nitrocellulose in 100 cc. of clear solution, and $B = \frac{4}{9}$ of the weight of original sample.

Solubility in acetone. This is determined by the same method as the solubility in ether-alcohol, except that acetone is used as solvent. If the volumetric reading is greater than 0.2, the determination is made gravimetrically.

KI-starch test or Abel test. A quantity of nitrocellulose is pressed in a clean cloth or wrung out in a wringer if it contains a large excess of water. The cake is rubbed up in the cloth until fine, taking care that it does not come in contact with the hands, spread out on clean paper trays, and dried in the air bath at 35° to 40°C. until the proper moisture content has been obtained. As it continues to dry, five successive samples are taken. The desired moisture content is that which will give condensation of moisture in diminishing amounts in the five test tubes used for these samples, ranging from an appreciable amount in the first tube to none in the fifth as the test progresses. The proper condition of nitrocellulose for the first sample is indicated when the nitrocellulose clings, after rubbing, to a spatula or to tissue paper which has been wrapped about the fingers. A sample of 1.3 grams is weighed out on a dispensing balance and transferred to a tube. The other tubes are filled approximately at 4- to 5-minute intervals until five tubes have been prepared. The tubes used should be 5½ inches long, of ½ inch internal diameter and ⅝ inch external diameter. During the test each tube is closed by a clean, tight-fitting cork stopper through which passes a tight-fitting glass rod equipped with a platinum holder for the paper. Corks are discarded after one test. The nitrocellulose is pressed or shaken down in the tube until it occupies a space of ⅝ inches. The KI test paper, about 1 inch in length and ⅜ inch wide, is hung on the platinum holder, and moistened on its upper half with a 50% solution of pure glycerine in water. The heating bath is carefully regulated at 65.5° ± 1°C., and is placed so that a bright reflected light is obtained. The time is taken when the tubes enter the bath. As the test continues, the line of demarcation between wet and dry test paper is kept abreast the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test paper marks the end of the test for each separate tube, the minimum test of any one of the five tubes being the heat test of the nitrocellulose. This discoloration is to be greater than that obtained at the same time by a blank test. Standard test paper is used in this test and is furnished by the Government. The standard water bath holds 10 tubes and is made long and narrow to reduce to a minimum the heating of the upper portions of the tubes. The tubes are immersed in the bath to a standard depth of 2.25 inches.

Heat test at 134.5°C. A sample of nitrocellulose is laid out in paper trays and dried for 4 or 5 hours at about 40°C., or is dried over night at room temperature and then further dried ½ hour at about 40°C., after which 2.5 grams are pressed into the lower 2 inches in each of two tubes of heavy glass about 290 millimeters long, of 18 millimeters outside diameter and 15 millimeters inside diameter, closed with a cork stopper through which a hole or notch 4 millimeters in diameter has been bored or cut. A piece of standard normal methyl-violet paper, 70 millimeters long and 20 millimeters wide, is placed in each tube, its lower edge 25 millimeters above the sample. When the constant-temperature bath has been carefully regulated at 134.5°C. ± 0.5°C., these tubes are placed in the bath so that no more than 6 or 7 millimeters of length project from bath. Examination of the tube is made by withdrawing about one-half its length and replacing quickly each 5 minutes after 20 minutes have elapsed. The minimum time, which will thus be a multiple of 5, in which the *violet* color of the test paper in either tube has completely turned to *salmon pink* will be reported as the time of test. For example, if the violet color is not completely changed in 25 minutes but is completely changed in 30 minutes, the time of the test is recorded as 30 minutes. The bath must be placed in a good light, with a suitable background. The standard normal methyl violet paper is furnished by the Ordnance Department.

Determination of nitrogen. A sample of approximately 1 gram of nitrocellulose, air-dried at a temperature not above 46°C., is placed in a ground-glass-stoppered weighing bottle (dimensions, approximately 50 millimeters high by 25 millimeters diameter) and dried for 1½ hours at a temperature ranging from 98° to 102°C., cooled in a desiccator, and weighed. The Du Pont nitrometer, with properly standardized compensating and reading tubes, is used for determination of nitrogen. For standard operation, room temperature must be between 15° and 32°C. The cup of the generating bulb is washed free from any nitrogenous impurities and the nitrocellulose is transferred to the cup; 20 cc. of nitrogen-free sulphuric acid, strength 94.5 ± 0.5%, is measured out into a graduate or small beaker. Small portions of the acid are run into the weighing bottle and transferred to the generating bulb until a sufficient quantity has been used to make an emulsion with the nitrocellulose. The mercury reservoir is lowered sufficiently to cause reduced pressure in the generating bulb. The upper stopcock is opened wide and the lower opened sufficiently to draw the nitrocellulose into the generating bulb. Successive rinsings with sulphuric acid are made until all of the nitrocellulose has been drawn in with the 20 cc. of acid. The upper stopcock is generally manipulated after the first time. Any air drawn into the bulb should be forced out, after which the upper stopcock is closed, the lower one remaining open, and the mercury reservoir adjusted just low enough to give a slightly reduced pressure in the generating bulb. The generating bulb is shaken gently, keeping the lower end in a fixed position until most of the gas has been generated. The mercury reservoir is adjusted so that the mercury in the generating bulb drops nearly to the lower shoulder, whereupon the lower stopcock is closed and the bulb is shaken vigorously for 3 minutes. The bulb is replaced on the rack with the lower stopcock open and the mercury reservoir adjusted until the mercury in the generating bulb is at approximately the same height as the mercury in the reservoir. This adjustment is for the purpose of bringing the pressure inside of the generating bulb to approximately one atmosphere so that the solubility of the nitric oxide gas in the sulphuric acid will not vary too widely. The lower stopcock is closed and the bulb shaken vigorously for an additional 3 minutes. The gas is now transferred to the measuring tube and the levels of the mercury in the compensating tube and the measuring tube are adjusted to approximately the same height. The gas is allowed to stand for about 20 minutes in order to permit equalization of temperature of the gas in the two tubes, and the mercury levels closely adjusted with a leveling device. The reading of the measuring tube is divided by the weight of the sample of nitrocellulose, giving the percentage of nitrogen in the nitrocellulose. The tare weight of the weighing bottle may be obtained before or after the test.

Ash. Two grams of dried nitrocellulose are placed in a recently ignited and tared crucible and treated with sufficient acetone containing 5% castor oil (by volume) to gelatinize it thoroughly. The nitrocellulose is then ignited and allowed to burn without applying heat until a charred residue remains, and finally it is thoroughly ignited, cooled, and weighed; the percentage of ash is then calculated. If preferred, the nitrocellulose may be digested with nitric acid, ignited carefully, and the ash determined.

Testing Smokeless Powder.[4] *Ballistic samples.* The number of containers required to make up the ballistic sample and the chemical and stability sample should be selected so as to be representative of the lot. If the weight of the samples required is less than 10 containers, a portion equal to one-tenth the weight of the required ballistic sample should be removed from each of 10 boxes and those 10 portions should be packed in individual airtight containers. It is desirable that the ballistic sample be taken not sooner than two weeks after the original packing.

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[4] See U. S. A. Specifications 50–12–3A, 50–12–5, 50–12–11A.

Chemical and stability samples. From each of the containers sampled for the ballistic tests, equal portions of the powder should be removed so as to have a sample for the chemical and stability tests of approximately the weight desired. Not less than 5 pounds of this sample should be set aside for 65.5°C. surveillance tests. The greatest cleanliness should be observed in handling the chemical and stability sample; handling it with damp or soiled hands should be avoided. The sample should be mixed thoroughly.

External moisture, air-dried. A sample of about 20 grams of the powder (or two whole grains, if a grain weighs more than 10 grams) is weighed accurately in a tared glass weighing bottle. It is dried in a vacuum oven (vacuum of at least 25 inches of mercury) at 55° ± 2°C. for 6 hours, cooled in a desiccator, and weighed. The loss in weight is calculated as the percentage of moisture in the sample.

External moisture, water-dried. A powder sample of about 20 grams (or two whole grains if a grain weighs more than 10 grams) is weighed accurately in a tared glass weighing bottle. It is dried for 6 hours at 100 ± 2°C. at atmospheric pressure, cooled in a desiccator, and weighed. The loss in weight is calculated as the percentage of moisture in the sample.

Diphenylamine. A sample of 5 grams of the powder is weighed accurately into a 250-cc. lipped beaker. The sample may be in whole grains if small enough to give a fair sample or in slices of medium or larger grains. Ten cubic centimeters of glacial acetic acid and twenty cubic centimeters of nitric acid (specific gravity 1.42) are mixed and poured on the powder. The beaker is covered with a watch glass and placed on a steam bath at about 95°C. for 1½ hours. It is necessary that the above quantities of acid be strictly adhered to by using either a pipette or graduate for the measurement. The powder dissolves completely with copious evolution of red fumes. The time and temperature given allows all red fumes to be dissipated without too much reduction of volume, and this is the end to be attained, since the nitro compounds have a tendency to crystallize out if the solution is evaporated too much or is allowed to stand too long after removal from the steam bath. Whenever such crystallization occurs results are slightly low.

Immediately after heating on the steam bath is completed, the solution is cooled, care being observed not to agitate, and poured into 75 cc. of distilled water which has been cooled to 15°C. in a 250-cc. glass-stoppered Erlenmeyer flask. The beaker is washed with water so that the solution, including washings, will be approximately 120 cc. The flask is shaken well for about 2 minutes and allowed to stand overnight.

The nitro compound is filtered on a Gooch crucible prepared by washing with 10% nitric acid and igniting. The nitro compound is washed six or seven times with water containing 1% of nitric acid, dried at 100° to 105°C. for 1 hour, cooled in a desiccator, and weighed. The crucible is placed in a small beaker, 10 cc. of acetone added, and allowed to soak for 15 minutes. The crucible is placed on a suction flask and washed with small quantities of acetone until nitro compounds are completely removed. The crucible is dried at 100° to 105°C. for 1 hour, cooled in a desiccator, and weighed. The loss in weight is calculated as the quantity of nitro compounds.

The factor for conversion of nitro compounds to diphenylamine, using the quantities of acid stated above, is 0.4259.

$$\%\text{ of diphenylamine} = \frac{\text{weight of nitro compound} \times 0.4259 \times 100}{\text{weight of powder}}$$

Graphite. The crucible used for the determination of diphenylamine is placed in a muffle furnace or in an inclined position over a gas burner and heated strongly until all carbonaceous material has disappeared. The crucible is cooled in a desiccator and weighed. The loss in weight is calculated as the percentage of graphite in the sample.

Total volatiles. The volatile determination is started as soon after receipt of the sample as possible. Any grains which have been handled should not be returned to the sample, except in special cases where the sample available is very small. The sample container is kept tightly closed. About 20 grains of all powders are used, regardless of caliber. A total of at least 2 grams is cut, taking approximately the same number of slices from each grain, after first cutting off and discarding about $\frac{1}{4}$ of the grain so that the slices used come from approximately midway between end and center of the grain. Each slice is cut so as to have as nearly as possible the same thickness at all parts of its area. The slices are cut either clear across the grain, giving a circular area, or just half across, giving a semicircular area. A sample of about 1 gram is weighed accurately into a tared aluminum can, approximately 50 millimeters high and 90 millimeters in diameter, provided with a tight-fitting lid and an aluminum stirring rod, the weight of which is included in the weight of the can. This sample is treated with 50 cc. of alcohol complying with United States Army Specification 4–10-18, and 100 cc. of ether complying with United States Army Specification 50–11–45. This mixture should be stirred frequently if it is desired to hasten solution, or the can should be covered and left under a bell jar overnight. When solution is complete the ether that has evaporated is replaced. The can is placed on a steam box or on a closed steam bath and a portion of the ether evaporated. The aluminum can should not be permitted to come in contact with steam or hot water. The amount of ether evaporated before the precipitation of the nitrocellulose determines the character of the precipitate; if too much ether is evaporated the precipitate will be gummy and difficult to dry; if too little ether is evaporated the precipitate will be sandy and cause bumping. The amount of ether to evaporate in order to obtain the desired fine, flaky precipitate depends upon the amount of nitrocellulose present and can be learned only by practice. When it is considered that the correct amount of ether has been evaporated, 10 cc. of distilled water is added. If the solution becomes opaque, indicating that the precipitation has started, water is added slowly with constant stirring to make a total of 50 cc. If the 10-cc. portion of water does not start the precipitation, a little more ether is evaporated and again 10 cc. of water is added. This process is repeated until a 10-cc. portion of water starts the precipitation and the precipitation is finished by adding sufficient water to make a total of 50 cc. If the precipitate seems too heavy, 5-cc. portions of ether are added and stirred until the precipitate becomes light and flaky. The ether is evaporated with constant stirring until there is no further danger of bumping, and then just to dryness. The can is transferred to an oven at 95° to 100°C. and the precipitate is further dried for $1\frac{1}{2}$ hours, cooled in a desiccator, and weighed. If the latter weighing does not check the former within 0.0005 gram, the $\frac{1}{2}$-hour dryings in the oven are repeated until the results check within this limit. A determination of nonvolatile residue at 95° to 100°C. is made on the quantities of water, alcohol, and ether used and the percentage of total volatiles is calculated as follows:

$$\text{percentage of total volatiles} = \frac{(A - B + C - D \times 100)}{E}$$

where A = original weight of can and sample; B = final weight of can and sample; C = weight of water, ether, and alcohol residues; D = correction in grams for volatilization of diphenylamine during the determination (25% of the diphenylamine content of the powder is allowed); and E = original weight of sample. The percentage of total volatiles, graphite, and diphenylamine is subtracted from 100 and reported as percentage of nitrocellulose in the sample.

Ash. From the remainder of the slices or grains a sample of about 1 gram is weighed accurately in a tared porcelain crucible. The sample is moistened with a small quantity of concentrated nitric acid and digested for 2 to 3 hours on a steam bath. The crucible is removed from the steam bath and heated over a Bunsen burner, cautiously at first to avoid loss. The crucible is finally placed in a muffle furnace, or over a gas burner, in an inclined position and partially covered with a lid, and heated strongly until all carbonaceous matter has disappeared; then it is cooled in a desiccator and weighed. From this weight the original weight of the crucible is subtracted and the result is calculated as the percentage of ash in the sample.

Compressibility. In this test, grains which are abnormal in shape or contain obvious flaws are not used. The ends of 10 normal grains of powder are cut so that new surfaces perpendicular to the length are exposed, and the length is equal to the diameter. The average length of these pieces is determined with a micrometer. Each grain is compressed between parallel surfaces, increasing the load slowly until the first crack appears. The load is removed and the grain is measured. The average reduction in length is calculated as a percentage of the average original length. If these 10 grains fail to pass this test, 20 more grains are subjected to the test. The average reduction in length is calculated in percentage of the average original length of the total 30 grains tested. This test is more completely described on page 129.

Heat test[5] *at 134.5°C.* Tests are made on five samples thus: 2.5 grams of sample are weighed out and each sample is placed in a test tube made of heavy glass, preferably pyrex, approximately 15 millimeters in inside diameter and 18 millimeters in outside diameter, and 290 millimeters long. Each sample should consist of grains as nearly whole as is consistent with a weight of 2.5 grams of sample. In sectioning grains to obtain the required weight, the grains are split longitudinally. A piece of standard normal methyl violet paper, 70 millimeters long and 20 millimeters wide is placed vertically in each tube, its lower edge 25 millimeters above the powder. The tubes are stoppered with corks through which holes 4 millimeters in diameter have been bored. The tubes are placed in a constant-temperature bath at 134.5 ± 0.5°C. so that no more than 6 or 7 millimeters of length project. Each tube is examined by withdrawing about one-half of its length and replacing quickly at 5-minute intervals after 55 minutes have elapsed. The time of the observation which reveals the test paper in any tube to be completely changed to a salmon pink color is recorded as the time of completion of the test. Heating is continued and report is made whether any sample of powder explodes in less than 5 hours. (Standard normal methyl violet papers and standards for salmon pink are secured from the Ordnance Department.)

TABLE 36

APPROXIMATE DIMENSIONS OF A FEW POWDER GRAINS IN MILLIMETERS

Caliber	Length	Diameter	Perforation diameter	Average web
16-inch	58	24	2	5
14-inch	42	18	2	4
12-inch	46	18	2	4
8-inch	33	14	1	2.5
155-millimeter	21	8	0.8	1.5
3-inch	15	7	0.6	1
75-millimeter	10	3	0.2	1
.30-inch	2	1	<0.1	single perforation
.45-inch pistol	Flakes, granular, free from dust.			

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[5] Compare page 238. In other cases this test is also run at 65.5° and 120°C. (see page 249).

Specifications for Smokeless Powder. In addition to comments already made which apply chiefly to straight nitrocellulose powder, specifications for smokeless powders vary with the type. Beyond what has been said of grain size, Table 36 gives the over-all size of a number of powder grains, and Table 37 the web sizes for many more.

The volatiles vary with the web size, as shown in Figure 34. Moisture (see Figure 35) varies both with web size and method of manufacture. For cannon powders, diphenylamine should be 1.0 ± 0.1%, with wider latitude for pistol powders, and the same figure is a maximum for rifle powders. Maximum ash is 0.4%, excluding metal and salts which may be used in small-arms or pistol powders. The heat tests for stability which have been given should be carefully noted.

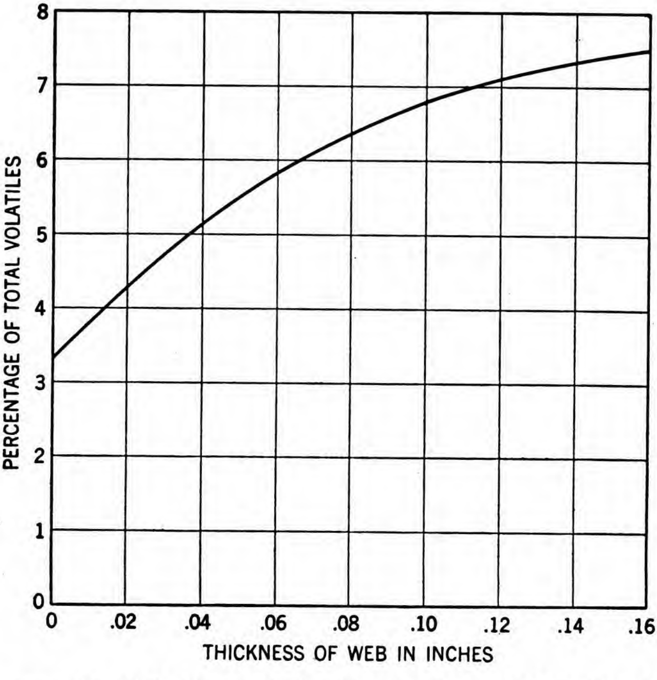
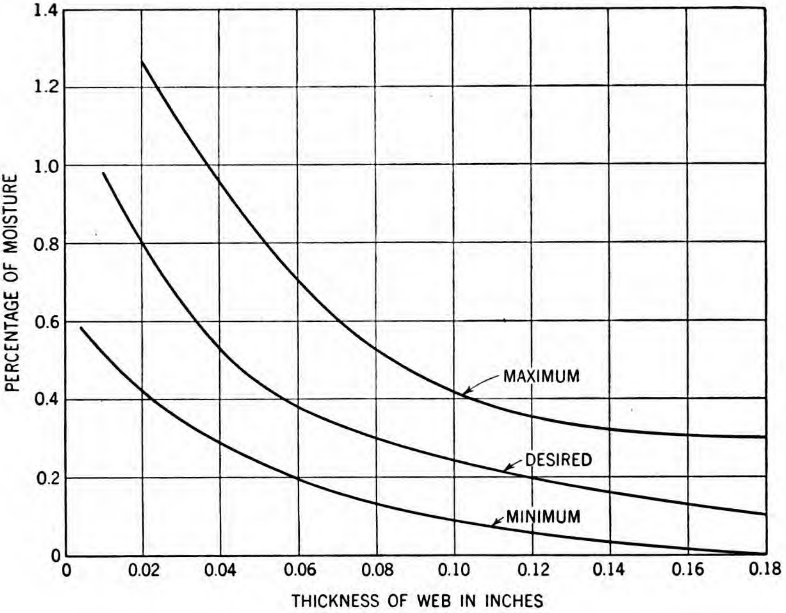


FIGURE 34: **Web Size and Volatiles for Pyrocellulose Powder**

Double-base Powders. *Composition.* The term "double-base" powder has been applied to powders containing nitrocellulose and nitroglycerine as the principal constituents. These powders as used by various military services usually contain from 60% to 80% of



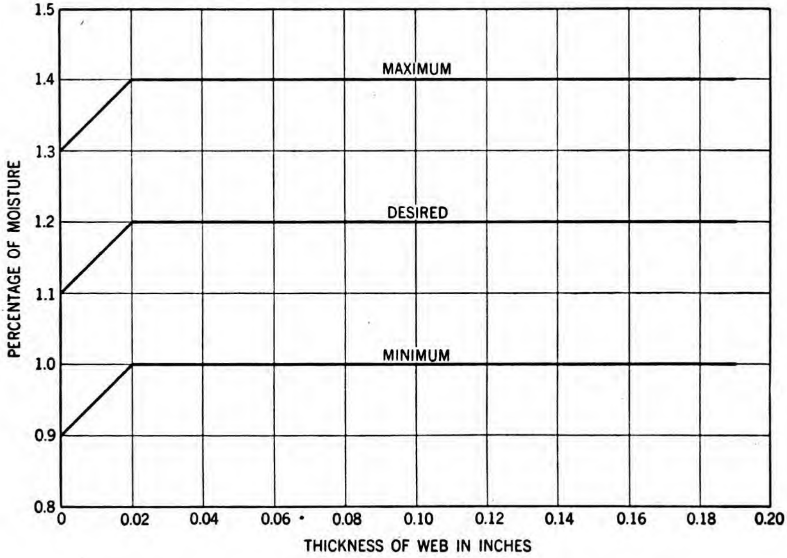


FIGURE 35: **External Moisture and Web Thickness**
(*Upper*) Air-dried, and (*lower*) Water-dried Pyrocellulose Powder.

nitrocellulose and from 40% to 20% nitroglycerine. Certain commercial powders used in sporting ammunition are of similar composition. The nitrocellulose used in double-base powders may be of the pyrocellulose type containing about 12.6% nitrogen or the more highly nitrated type containing above 13.0% nitrogen, commonly referred to as guncotton. Small percentages of inorganic salts such as potassium or barium nitrate are often used in double base powders, these salts serving the purpose of reducing flash or rendering the powder more ignitable. When the percentage of nitroglycerine in the powder composition is small or when the powder is to be extruded, it is customary to use a volatile solvent to colloid the powder. The volatile solvent may be omitted with compositions that contain a high percentage of nitroglycerine and are granulated in thin sheets or disks by rolling, since nitroglycerine is in itself a solvent for nitrocellulose, and the rolling operation colloids the powder to the desired degree.

TABLE 37

WEB RANGE FOR SOME PYRO POWDERS

Weapon	Model	Projectile Wt. Lbs.	Web Size in.
37 mm.	1916	1.234	0.013
37 mm. A.A.	MI.	1.25	0.021 –0.0227
37 mm. Gun	S.A. Tank.	1.25	0.0176
75 mm.	1917	11.72	0.019 –0.027
75 mm.	MI.	14.3	0.031 –0.0322
3″ F.G.	1905	15	0.0238–0.0264
3″ A.A.	M_1M_3	12.7	0.036
105 mm. A.A.G.	M_1	33	0.037
6″ Gun	1908	108	0.064 –0.067
155 mm. Gun	M_1E	95	0.0535–0.0545
155 mm. Howitzer	1918	95	0.0272–0.033
8″ Howitzer	1920 E	200	0.0455–0.0462
12″ Gun	1895	1070	0.1248–0.138
12″ Mortar	1912	700	0.0712–0.078
14″ Gun	M_{11}	1200	0.142 –0.1435
16″ Gun	1919	2340	0.168 –0.173
16″ Howitzer	1920	2100	0.094 –0.095

Characteristics and use. The energy content of nitroglycerine is considerably higher than that for nitrocellulose and, therefore, powders containing nitroglycerine have higher potential than straight nitrocellulose powders, the difference increasing with the percent of nitroglycerine present. The double-base powders are also more readily ignitable and have a higher rate of burning. These characteristics have led to the use of such powders in trench mortars, where especially rapid burning is required. They are also used in certain high-velocity weapons where the high potential of the double-base powders is favorable.

Inspection tests. In the inspection of the double-base powders, the usual chemical-stability and ballistic tests are conducted. Since the chemical and ballistic test requirements vary with the various types of powder but the stability requirements are common to all, the latter requirements only are given.

The heat test at 120°C. is used to determine stability. All powders are required to withstand this test for at least 40 minutes without changing the color of the test paper, and to show no evidence of fumes in 60 minutes. The procedure for this test is as follows: 2.5 grams of the sample are placed in each of two tubes of heavy glass having the following approximate dimensions: length, 290 millimeters; outside diameter, 18 millimeters; inside diameter, 15 millimeters. Each of the tubes is closed with a cork stopper through which has been cut a hole or groove of about 2 millimeters diameter. A piece of standard normal methyl violet paper 70 millimeters long and 20 millimeters wide is placed in each tube so that its lower edge is 25 millimeters above the powder. These tubes are placed in a bath at a temperature of 120.0 ± 0.5°C. so that no more than 6 or 7 millimeters of each tube project outside the bath. The tubes may be examined by withdrawing them about one-half their length outside the bath and replacing them immediately. The tubes are examined every 5 minutes after the first 20 minutes have elapsed. The time in which the methyl violet paper has turned completely to standard salmon pink in either tube is reported. After 60 minutes the tubes are examined against a white background for evidence of fumes.

E. C. Powder. *Composition and use.* This propellant is generally used for loading blank cartridges and hand grenades. It consists of semicolloided nitrocellulose granulated with inorganic nitrates.

Manufacture. The main point observed in manufacture is proper incorporation and mixing of all ingredients. This process is usually conducted by means of a wheel mill in a manner somewhat similar to that used for black powder. Nitrocellulose of approximately 13.15% nitrogen is mixed with about 16% of a mixture of equal parts of potassium nitrate and barium nitrate, together with a small amount of diphenylamine and a pink or yellow coloring matter. The powder mixture is granulated by adding a mixture of water and a suitable solvent to the material in a revolving drum in such a manner that it forms small rounded grains. The nitrocellulose in these grains is only partially colloided, acting as a binding material and hardening the surface of the grains as the solvent is removed.

Granulation. The granulation of E. C. powder is such that the powder will pass a 12-mesh and remain on a 50-mesh screen. A tolerance of 3% is permitted; that is, 3% of the powder may remain on the 12-mesh screen, but the material remaining on the screen must pass a 10-mesh screen, and 3% may pass a 50-mesh screen.

Heat test at 134.5°C. The powder must not turn normal methyl violet paper to a salmon pink color in less than 30 minutes and must not explode in less than 4 hours in this test.

Smokeless Powder as an Explosive. The characteristics of smokeless powder as an explosive are essentially those of pyrocellulose, which has been described, modified by the other materials which may be present. Smokeless powder does not detonate on ignition—that, of course, would be undesirable—but it should be remembered that smokeless powder can be detonated. A fall of 30–45 centimeters of the 2-kilogram weight will detonate it. Its explosion temperature is from a little below to much below that of nitrocellulose (2,710°C.) and may run from 2,400°C. down to 1,940°C. Its explosive strength, measured by tests for *brisant* explosives, may be from 25% under to slightly more than nitrocellulose for nitroglycerine powders; its Q_v = 1,100 to 1,300 Calories per kilogram, and its lead-block expansion is 420 cc.

Discussion Questions and Exercises

1. Tabulate as many properties of the colloidal gel, smokeless powder, as you can, and compare with nitrocellulose.

2. Tabulate the total time required to prepare a batch of smokeless powder.

3. Prepare a flow sheet, from memory, for smokeless powder.

4. Make the usual explosives calculations for the formulae on page 210.

5. Determine the weights of alcohol and ether necessary to make 2,000 pounds of smokeless powder and estimate the recovery.

6. Name some other materials which might have possibilities as stabilizers for smokeless powder to replace diphenylamine. What properties should they have?

8. From the table of approximate sizes and the specifications for grains in Chapter 7, tabulate some exact dimensions for various smokeless powder grains.

9. Be sure that you thoroughly understand the use of the Du Pont nitrometer.

10. Prepare a complete but synoptic outline of the examination of smokeless powder, including grain characteristics, for each type of powder.

11. Elaborate the manufacture of E. C. powder in terms of the previous material.

12. Report on other methods of manufacturing smokeless powder.

CHAPTER 12

T.N.T., Nitro Compounds in General, and Other Explosives, Including Gases

The Cyclic Nitro Compounds. These compounds include the most important military high explosives, but they have also some general application. Trinitrotoluene (1:3:5)—also known as triton, trotyl, trilite, and by a variety of other names—has been an important military explosive since 1904, and is still quantitatively most important. Nitration products of benzene, metaxylene, phenols, anilines, and their substitution products are useful, as well as others. Nitronapthalenes have some applications, among others as stabilizers for nitrocotton, but relatively more is required than of diphenylamine; and in dynamites. Nitrophenanthrenes, nitroanthracenes, and nitro derivatives of more complex hydrocarbons are known, although even from the laboratory standpoint exact identification of complete series of some of the nitro derivatives of the higher hydrocarbons is still uncertain, and they have no large practical use.

Trinitrobenzene (1:3:5) is a more powerful and in many ways more desirable explosive than T.N.T., and would be very useful, were it not for the fact that it is so difficult to prepare by direct nitration. It is practically impossible to manufacture trinitrobenzene economically on a large scale in that way, and it is usually made indirectly from toluene. It is informative to compare the properties of the nitro derivatives of benzene, toluene, and xylene from the standpoint of ease of nitration, sensitivity, and power as explosives. Table 38 presents that comparison and also shows some comparison of these properties with structure.

In our descriptions of these explosive materials, we shall use the following general outline, which is suggested to the student for his study: (*A*) Chemical characteristics of the substance; (*B*) method of preparation, commercial and laboratory; (*C*) explosive reaction, and general explosive characteristics as previously outlined, page 23; (*D*) Government and/or trade requirements; (*E*) standard tests; (*F*) uses.

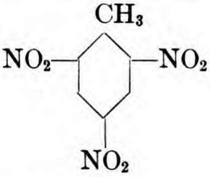
TABLE 38

COMPARISON OF CYCLIC NITRO COMPOUNDS

	Sensitivity cms. for 2 Kg.	Lead Block Expansion, cc. for 15 g.	Velocity of Explosion m. per sec.	Ease of Nitration
Nitrobenzene	> 180			50°C.
Dinitrobenzene 1:3	120	↓	↓	80°C.
Trinitrobenzene 1:3:5	40–50	480	7441	1 day > 100°C.
Nitrotoluene ortho or 2				50°C.
Dinitrotoluene 2:4	↑	↓	↓	80°C.
Trinitrotoluene 2:4:6	57–90	452	7028	3 hrs. at 100°C.
Mononitrometaxylene 2				similar to toluene, but more easily.
Dinitrometaxylene 2:4	↑	↓	↓	
Trinitrometaxylene 2:4:6	170	450	7000	
Trinitronaphthalenes	175	166	about 3,000	80°C.

Calculate and compare Qv, Te, *f*, etc.

Chemical Characteristics of T.N.T. Pure T.N.T.—1:3:5, or 2:4:6 as it is sometimes numbered. The compound meant is always



—is a monoclinic crystalline material, colorless to pale cream, with a melting point of 80.7°C. Commercial grades are darker. United States Army specifications give two grades: I of setting point (see page 260) 80.2°C. minimum, II of setting point 76.0°C. minimum. Grade II can be prepared directly by the nitration process; Grade I must be purified as will be indicated. T.N.T. has a specific gravity of 1.654 and is practically insoluble in water but crystallizes excellently well from alcohol, in which it is very soluble hot and slightly cold, and from other organic solvents. It boils at 240°C. with explosion, but can be distilled under diminished pressure.

The methyl group in T.N.T. is reactive and will undergo many condensation reactions in which two hydrogens are lost by the formation of water with oxygen from another compound, for example nitroso compounds, and aldehydes,

$$(\mathrm{NO_2})_3\mathrm{C_6H_2CH_3} + \mathrm{O{=}N{-}R} \rightleftharpoons (\mathrm{NO_2})_3\mathrm{C_6H_2CH{:}N{-}R} + \mathrm{H_2O}$$

$$\overset{\mathrm{HOH}}{\rightleftharpoons} (\mathrm{NO_2})_3\mathrm{C_6H_2CHO} + \mathrm{RNH_2}$$

These reactions are sometimes highly exothermic and the presence of such materials may cause explosions. T.N.T. and most of the nitrohydrocarbons form very sensitive explosive addition products with alkali, and their presence also is to be avoided.

T.N.T. is definitely toxic, especially for some people, and ventilation and personal cleanliness are necessary in handling to avoid inhalation of vapor and dust and absorption through the skin.

Manufacture of T.N.T.[1] The essential steps in the principal process of manufacture are:

A. Production of mononitrotoluene from toluene.
B. Production of dinitrotoluene from mononitrotoluene.
C. Production of T.N.T. from dinitrotoluene.
D. Washing the trinitrotoluene free of acid.
E. Purification by one of the processes described.
F. Granulation, screening and drying.

Nitration. Several processes are used, for example: (1) The one-stage process, where a large excess of strong mixed acid is used and the temperature gradually raised, with the result that trinitrotoluene is produced in the one process without transfer or separation of spent acid from intermediate products. (2) The two-stage process, where either mono- or dinitrotoluene is produced in the first stage and trinitrotoluene in the second. (3) The three-stage process, where by the use of three different acid mixtures and different conditions of temperature and the like, mono-, di-, and trinitrotoluene are successively produced.

The one-stage and two-stage processes have been superseded by the more practical and more economical three-stage process. A general description of the three-stage process follows:

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[1] U. S. A., TM 9–2900, *Military Explosives.*

First stage. The normal charge used in the manufacture is 1,300 pounds of toluene. The first step in the nitration is accomplished by running into the nitrator approximately 1,200 pounds of mono spent acid. The purpose of adding the spent acid is to provide a very weak charge as a bottom layer so as to prevent stripping the nitrating acid of nitric acid and also to raise the toluene level so that it will come in contact with the cooling coils. If this spent acid is not added, stripping of the nitrating acid is likely to occur, which results in a charred mononitrotoluene. The amount of acid used in the mononitration is based on a ratio of 1 part of toluene to .9 parts of nitric acid. The composition of the mixed acid is 76% sulphuric acid, 23% nitric acid, approximately, water being about 1%. The agitation used during this nitration should be slow enough to prevent mixing of the toluene and the acid; that is, a separating line between these two components should be maintained throughout the nitration. The acid is added through a spider distributor and the temperature maintained at 50°C. during the addition of the first 2,000 pounds, between 50° and 55°C. for the next 4,000 pounds, and at 55°C. for the balance of the charge. The nitration is accomplished by the acid dropping through the toluene. After all the acid has been added, the charge is cooked for 10 minutes, cooled to 45°C., then allowed to settle for 15 minutes, and the acid charge is run off. The acid used in this nitration, where a plant is in continuous operation, is made up by fortifying the spent acid from the dinitration.

Second stage. This stage consists in nitrating the mononitrotoluene to dinitrotoluene. The mononitrotoluene obtained in the first stage is blown from the mononitrating house to the ditrinitrating house and placed in the ditrinitrator. The charge is first cooled to 45°C. The mixed acid used in this nitration is usually a fortified acid made by adding nitric acid to a spent acid from a previous trinitration. The strength of the acid approximates that used in the mononitration, the nitric acid ratio being the same as for the mononitration. The acid is added to the mononitrotoluene and the temperature allowed to increase by 3° steps until it has reached a temperature of 80° to 83°C. It is held at this point for the completion of the nitration. After all acid has been added, the charge is cooked for 30 minutes and cooled to 60°C., settled for 30 minutes, and the spent acid discharged. This spent acid is forwarded to the fortifying house for the addition of nitric acid so that it may be used in the next mononitration.

Third stage. In this stage, the dinitrotoluene is nitrated to trinitrotoluene. It is this stage of manufacture that offers the most difficulty, and extremely strong acids are required to obtain a complete nitration. It is necessary to employ an anhydrous acid. Approximately 3,500 pounds of fuming sulphuric acid is added to the dinitrotoluene oil. This acid is added gradually, the temperature being allowed to rise in 3° steps until a temperature of 80°C. has been reached. As soon as the fuming sulphuric has been added the mixed acid is started. The mixed acid has a composition of 57% nitric and 43% sulphuric, approximately. The nitrating temperature in this stage is 85°C. at the start with a gradual rise in 3° steps until it reaches 104°C. From this point the nitration is continued until a test of the oil shows it has a freezing point of 72°C. or higher. Normally it requires 3 hours of nitration after all the acid is in to obtain this setting point. After this, the charge is cooled to 100°C. and allowed to settle for 30 minutes, after which the spent acid is sent to the fortifiers and the trinitrotoluene oil to the neutralizing house.

Yield. Humphrey[2] states that contrary to usual belief, yield of T.N.T. from the second or dinitration at a given temperature is not a function of the water content of the mixture (except that too strong an acid tends to oxidize the material and in this manner lowers the percentage of yield), but is rather dependent upon the proper low temperature during nitration.

The mononitration yields a product containing a mixture of about 4% of the meta nitrotoluene in addition to the ortho and para isomers. The subsequent nitration changes the meta mononitrotoluene chiefly into the beta and gamma trinitrotoluenes, which differ from the alpha form in chemical properties and are regarded as impurities. Small amounts of other isomers of trinitrotoluene have also been identified in the product of the complete nitration of toluene. Depending upon the completeness with which the last nitration is performed, there may be either a large amount of dinitrotoluene present if improperly carried out, or a relatively small amount if the nitration is correctly done.

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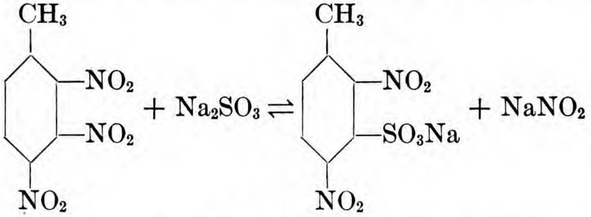
[2] Humphrey, *J. I. E. C.* 8, 998 (1916).

In addition to these impurities, there may also be such bodies as tetranitromethane, which possesses the undesirable property of lowering the solidification point of the pure alpha T.N.T. If the nitration has been properly carried to completion, not more than 4% beta and gamma T.N.T. should be present. This condition is not usually attained under manufacturing conditions and it is therefore necessary to recrystallize the T.N.T. or to purify it by other means in order that the impurities may be eliminated, and a product obtained having the required solidification point for grade I T.N.T. (80.2°C.).

Purification. *Process and equipment.* The crude trinitrotoluene, which, due to the temperature of nitration, is in the form of an oil, is run from the nitrator into neutralizing tubs which have the shape of a cone at the bottom. At the apex of the cone a gateway valve for regular discharge from the tub is provided. Both steam coils for heating and air coils for agitation are provided. Wash water is drawn off by means of suction through a suitable pipe which reaches the tub near the top and extends along the side wall to about 2 feet from the bottom. A small quantity of sodium sulphite can be used to assist in the purification at this point, although it is not necessary to do so. Washing is carried on until no acidity is shown by tests using litmus paper. The neutral T.N.T., in the form of oil, is now pelleted by running it into cold water for transportation to the graining house, or it can be transported in the molten condition to suitable storage tanks through heated pipe lines. If pelleted, these pellets are transported to storage tanks as above mentioned, and again melted before running into the crystallizing kettles. The storage tanks are kept at an approximate temperature of 95°C. and are provided with a gateway screw valve from which the molten charge is drawn off into the graining kettles. These kettles are made of cast iron in one piece, and the junction of the bottom and the side walls is rounded so that plows can scrape the T.N.T. loose from the sides. The lower part of the kettle is fitted with a jacket into which steam or cold water may be discharged. As the plows are started, the charge cools down and the crystals begin to form on the sides; these increase until the whole mass becomes plastic. During the operation all moisture is driven off and the T.N.T. produced is in a fine crystalline condition. It is usually better than grade II; that is, it has a melting point above 76°C. If it is desirable to obtain T.N.T. of grade I, it may be recrystallized from sulphuric acid or another suitable solvent, or treated with sodium sulphite.

Crystallization from sulphuric acid. The fine crystals produced in the graining kettles are dissolved in hot sulphuric acid, usually weight for weight, and cooled. The purified crystals thus settling out are washed free from acid and regrained to such degree of fineness as to pass United States Army specifications. The crude material held in sulphuric acid is accumulated until such time as the amount warrants separate purification.

Sulphite treatment. The sodium sulphite treatment may be applied by taking the fine crystals from the graining kettles and placing them in bins or cars which are equipped with a Filtros bottom. These bins or cars are given one hot-water washing, then four washings with the 5% solution of sodium sulphite, then one warm-water washing followed by sufficient cold-water washings to remove the last traces of the red color which is formed in the treatment. The purified crystals thus obtained can be dried, sieved, and packed, or regrained, as may be necessary to meet specifications. This method of purification is based upon two facts. First, in the nitration of toluene some meta-substituted impurity is always produced. Second, the meta-oriented nitro group in a polynitro cyclic compound is more reactive than others, and will undergo double decomposition reactions, in this case with the formation of water soluble sulphonates; for example:



Laboratory Preparation of T.N.T. The commercial process may be conducted on a laboratory scale as follows:

Using 20% fuming sulphuric acid and commercial nitric acid, 95%, specific gravity 1.5, (*a*) prepare 100 cc. of mixed acid containing 76% H_2SO_4, 23% HNO_3, and approximately 1% of water; (*b*) prepare 50 cc. of mixed acid containing 43% H_2SO_4 and 57% HNO_3.

Mononitration. Put in a small beaker on a water bath 10 grams of the 76–23 mixture, which is to represent spent acid, and add 10 grams of toluene. Bring the temperature to 50°C. Through a dropping funnel just above the surface, add 50 grams more of "spent acid," slowly raising the temperature to 55°C. Keep at 55°C. for 10 minutes after all the acid is added. Cool to 45°C., allow to settle for 15 minutes, and then separate the acid in the separating funnel.

Dinitration. In a beaker on a water bath bring the mononitrate to a temperature of 45°C. Through a dropping funnel add 50 grams of the 76–23 acid mixture, meanwhile raising the temperature slowly by 3° steps until a temperature of 83°C. is reached. Keep at 83°C. for 30 minutes after addition of acid, cool to 60°C. and allow to settle for 30 minutes. Separate in a funnel.

Trinitration. To the dinitrotoluene oil in a beaker over a small gas flame, add slowly through a dropping funnel 30 grams of fuming sulphuric acid (20%), raising the temperature by 3° steps to 80°C. Now through the funnel add 30 grams of 57–43 mixed acid, raising the temperature by 3° steps until it reaches 104°C. Hold at this temperature for 3 hours, or until the oil has a freezing point of 72°C. or higher. Allow the contents of the beaker to settle at 100°C. for 30 minutes and separate the oil. All quantities here can be multiplied by any constant factor.

Purification. Wash the oil with boiling water with stirring until the wash water is neutral to litmus. Then add cold water slowly with good stirring so that the T.N.T. separates in pellets. Weigh and compute the yield. Determine the melting point.

Take one-quarter of the yield and dissolve in an equal weight of hot concentrated sulphuric acid. Cool, separate the crystals using a Gooch crucible, and wash free from acid, using cool water. Determine the melting point.

Take one-quarter of the yield and wash once with hot water, four times with 5% sodium sulphite solution, once with warm water, and then with cold water until free from the red color formed by the treatment. Determine the melting point.

The determination of the solidification point of T.N.T. (see page 261), requires a 50-gram sample. Pure T.N.T. in closed bottles offers no hazards on keeping if it is protected from possibility of detonation.

T.N.T. as an Explosive. In small quantities, on ignition, T.N.T.

burns; but sudden heating will cause detonation, likewise the accumulation of heat in burning large quantities. T.N.T. is one of the most stable of all high explosives and its handling is restricted by few conditions. It requires a fall of up to 130 centimeters of the 2-kilogram weight to explode it. On the other hand, it is a powerful high explosive, producing a lead-block expansion of 285 cc. (10 g.); Q_v = 656 Calories per kilogram; T_e = 2,419°C. It is detonated by such usual detonators as blasting caps, requiring at least a No. 6 for full power, and, for full efficiency in the cast form, the use of a high-velocity initiator as tetryl.

TABLE 39

SPECIFICATIONS FOR T.N.T.

Characteristic	Grade I	Grade II
Color	light yellow to buff	same
Setting point, minimum	80.2°C.	76.0°C.
Moisture	0.10%	same
Acidity	0.10%	same
Insoluble matter	0.10%	same
Insoluble matter retained on No. 40 sieve	0.01%	same
Grit	none	same
Granulation	Crystals: Not less than 95% shall pass No. 14 sieve. Flakes: Average thickness $<.025$ inch., none > 0.04 inch.	
Maximum lot	100,000 pounds	

T.N.T. has an oxygen deficiency, and can explode in several ways (page 99), in common with all the compounds of this group. T.N.T. yields dense clouds of soot on explosion, whereas some of the others have at least enough oxygen to yield entirely gaseous products. Mono- and dinitrotoluenes are added to other explosives for reducing temperature of explosion, to make flashless and permissible explosives.

Analysis of T.N.T.[3] Government specifications for T.N.T. are found in Table 39. Prescribed analysis procedures follow.

Sampling. Select at least 1 box from each 5,000 pounds of packed T.N.T., in no case less than 10 boxes, so as to be representative of the lot. Remove from different parts of each selected box enough of the material to give a sample of about 1 pound; mix this sample thoroughly and place an 8-ounce portion in a bottle so labeled that the box from which the sample was taken can be easily identified. The remainder of each primary sample should weigh about 8 ounces. Mix these remainders thoroughly, and quarter the blend successively until a composite sample of about 1 pound is obtained. Place all samples in tightly stoppered bottles and label each so as to show the name of the material, manufacturer, plant, purchase order and number of pounds in the lot. All acceptance tests are made on the composite sample representative of the lot. Hold the primary samples for possible future examination should the composite sample fail to meet the requirements.

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[3] U. S. A. Specifications 50–13–5C.

Setting point. Place approximately 50 grams of the sample in the inner tube from a solidification-point apparatus. (See both Figure 36 and the description under picric acid, page 271. The same apparatus is used for both of these determinations.) Heat the tube and sample in an oven at 95° to 100°C. for two hours, then place in the solidification-point apparatus. Insert thermometers as shown in the sketch so that the bulb of one, a standardized thermometer calibrated in graduations of 0.1°C. for total immersion, is approximately in the center of the molten T.N.T., and the bulb of the other, a correction thermometer graduated in 1°C., is about one centimeter from and adjacent to the middle of the exposed mercury column of the thermometer immersed in the sample. Stir the sample thoroughout the determination, making approximately 120 complete up and down motions of the stirring rod per minute. Closely watch the thermometer immersed in the sample to determine when the temperature of the sample ceases falling and begins to rise due to the heat of crystallization. Note the temperature of the sample every 15 seconds until the maximum is reached and record this temperature as the uncorrected setting point. Record the reading on the correction thermometer as the average temperature of the exposed mercury column. Calculate the correction for emergent stem as follows:

$$\text{Correction (°C.)} = n(T - t)(0.000159)$$

where n = number of degrees in exposed mercury column, T = uncorrected setting point, and t = average temperature of exposed mercury column. Calculate the setting point of the sample by adding this correction to the uncorrected setting point.

Moisture. Weigh approximately 5 grams of sample in a glass weighing dish or suitable weighing can. Dry the sample for 8 hours in a vacuum desiccator containing sulphuric acid and weigh. Calculate the loss in weight as percentage of moisture.

Acidity. Weigh approximately 10 grams of sample, melt, shake with approximately 100 cc. of neutral boiling water, and allow to cool. Decant the water and retain. Remelt the sample and extract again with 50 cc. of neutral boiling water. Combine the water extracts, cool, and titrate with a solution of sodium or potassium hydroxide, not stronger than $N/10$, using phenolphthalein as indicator. Calculate the acidity as percentage of sulphuric acid in the original sample.

Insoluble matter. Dissolve a weighed portion of approximately 10 grams of the sample in approximately 100 cc. of benzene or ethyl alcohol. Filter the solution through a tared Gooch crucible. Wash the crucible and residue thoroughly with solvent, dry at 100°C., cool and weigh. Calculate the gain in weight as percentage of benzene or alcohol-insoluble matter.

Insoluble matter retained on No. 40 sieve. Transfer a 100-gram portion of the sample to a beaker and dissolve in benzene or ethyl alcohol. Pour the solution through a No. 40 U.S. standard sieve and transfer any insoluble matter from the beaker to the sieve by means of a jet of the solvent. Wash the insoluble matter on the sieve thoroughly by means of a jet of the solvent. When no more insoluble matter passes through the sieve, dry the sieve and residue remaining on it at 100°C. for one hour. Transfer the dry residue to a piece of paper and then to a tared glass weighing dish. Weigh the dish and from the increase in weight calculate the percentage of insoluble matter in the sample retained on the sieve.

Grit. Transfer the residue, obtained as directed in the paragraph above, from the weighing dish to a smooth glass slide. Rub the material on the glass by exerting pressure with a smooth steel spatula blade. Note whether particles of grit are present as indicated by lack of uniformity and the persistence of a scratching noise when pressing and rubbing of the material on the glass is continued.

Granulation. If the material is in a finely crystalline form, place a metal washer or porcelain crucible lid and a weighed portion of 100 grams of the sample on a No. 14 U.S. standard sieve, attach a bottom pan and cover, and shake the assembly for 3 minutes. Weigh any material retained on the sieve and calculate the percentage passing through the sieve.

If the material is in the form of flakes, measure, by means of a micrometer accurate to at least 0.001 inch, the thickness of each of 100 flakes taken at random from the sample. Note the maximum thickness and calculate the average thickness.

Packing. T.N.T. is packed in (1) rectangular wooden boxes of 50 pounds capacity, complying with the requirements of Interstate Commerce Commission Container Specification No. 14, or in (2) solid fiberboard boxes of 50 pounds capacity complying with Specification 50–61–5, or in (3) fiber drums (approximately 130 pounds capacity) complying with Specification 50–61–4. Wooden or solid fiber boxes are lined with bags having sift-proof bottoms and seams, made from paper at least equal in strength and moisture resistance to the so-called sandwich paper made from two sheets of 30-pound No. 1 Kraft laminated with 30 pounds of asphalt. When the T.N.T. is packed in fiberboard boxes, an additional sheet of protecting paper is provided to cover the entire top of the container. Closure of the fiberboard box is accomplished by coating the entire contact surfaces of the closing flaps with suitable vegetable or animal glue. Precautions are taken so that moist glue does not come in contact with the liner or bag.

Uses. T.N.T. may be regarded as the equivalent of 40% dynamite (sometimes 50%), and can be used under water. It is also used for the detonating fuse known as Cordeau Bickford. For military purposes, T.N.T. can be used for all types of bursting charges, including armor piercing, although it is slightly too sensitive for that purpose and has been replaced by ammonium picrate.

T.N.T. is a relatively expensive explosive. It does not compete seriously with dynamite for general commercial use, but in half-pound blocks it is extensively used for military engineering purposes. For shells it has the advantage that because of its low melting point, it can be melted and loaded by pouring.

Even for military purposes, because of cost, the United States government during the First World War authorized the use of amatol, which is a mixture of T.N.T. and ammonium nitrate, and although increasing supplies of toluene make this no longer so important, 50–50 amatol is still used rather than T.N.T. for shells above 3 inches, and 80–20 for the largest sizes. T.N.T. is also used in mixtures with many other explosives, such as P.E.T.N.; and trimethylenetrinitramine (hexogen and cyclonite), both of which are more powerful than T.N.T.

Amatol. Amatol is more insensitive than T.N.T. but 50–50 amatol is about the same strength, while 80–20 is slightly lower in velocity and *brisance.* The amount of smoke is decreased, and 80–20 produces a white smoke.

Manufacture of 50–50 amatol.[4] The ammonium nitrate as received may contain some moisture and must be dried to a moisture content of not more than .25%. It may also be found that caking has occurred in the barrels or drums in which it has been shipped. To break up the lumps it is often necessary to run the material through a crusher and then dry it to the proper moisture content. After drying, the material is screened to remove any foreign material with which it may have become contaminated. It is now ready for addition to molten T.N.T. The speed of adding ammonium nitrate to T.N.T. can be increased greatly if the ammonium nitrate can be added while it is still hot. It must be added at a rate so that no solidification of the molten T.N.T. takes place in the melting kettle. Proportions for use in mixing 50–50 amatol range from 45% to 55% ammonium nitrate. This variation is permitted to take care of the various granulations, fine material requiring more T.N.T. than coarse material. Temperature of the mixture when it is ready for pouring in the shell is 80° to 85°C.[5]

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[4] U. S. A., TM 9–2900, *Military Explosives.* U. S. A. Specifications.

[5] The melting point of an explosive is a physical property which is frequently of importance in several ways. In the case of nitroglycerine, which is exceptional, the problem of freezing at low temperatures, which has been discussed, presents itself. In general, within limits, the velocity of explosion and therefore, the violence of brisant effects, increases with increasing density. In practice this optimum density is obtained in the loading operation. For an explosive with a reasonably low melting point, in general below 100°C., this can be attained by pouring the explosive as a liquid and allowing it to solidify. Attention must be paid to the contraction on solidifying. The pouring method of loading is a simple and desirable operation. T.N.T. and various of its mixtures, picric acid, and other compounds lend themselves to this. Where it is not possible, loading must be by tamping or extrusion, either of which operation is more complicated,

Manufacture of 80–20 amatol. Eighty-twenty amatol is a plastic mass resembling wet brown sugar and cannot be loaded by the casting method. The principal difficulty experienced with 80–20 amatol is to obtain ammonium nitrate which has proper granulation. With very fine material, plasticity of the mass is such that after loading the density falls below the point desired, namely, not less than 1.38. With coarse material, molten T.N.T. is not completely absorbed and a relatively large amount leaks out in the extruding operation; the result is then a charge of low density. It is therefore essential that granulation be such as to give a mixture which will not permit leaking of T.N.T. and which will be sufficiently plastic to consolidate well from the extruder. It has been found that a mixture of coarse and fine material is the most suitable for this operation. Granulation requirements are: through a No. 10 U.S. standard sieve not less than 99%; through a No. 10 on No. 35, 32% to 48%; through a No. 100, 15% to 30%.

Preparation of 80–20 amatol is conducted in a mixing kettle having a capacity of about 500 pounds of amatol. The correct amount of ammonium nitrate is added to the kettle and heated to the point where solidification of T.N.T. will not occur. When the ammonium nitrate has been raised to at least 90°C., molten T.N.T. is added and the charge is thoroughly mixed for 15 minutes. At the end of this time it is transferred to the extruding machine from which it is forced into the shell by means of a screw working inside of a steel tube. This machine is counterweighted so that the material is forced into the shell under a definite pressure.

Inspection of raw materials. Ammonium nitrate and T.N.T. used in preparation of amatol must conform to United States Army specifications governing these materials, as impurities in both have harmful effects on the resulting product. Oily impurities in the T.N.T. will cause exudation or leakage, while impurities in ammonium nitrate, such as pyridine, cyanide, and the like, will cause formation of gas or frothing, resulting in probable cavitation in the shell. Methods of analysis governing inspection of these materials are given elsewhere (page 198).

Samples. Samples should be taken from the mixer while the stirrers are rotated, as the T.N.T. and ammonium nitrate have a tendency to segregate. It is desirable to take the sample in an aluminum or thin sheet-iron vessel, a circular piece of stout cardboard being placed in the bottom. To obtain concordant results with duplicate analyses, experience will show that extreme care must be taken with the samples.

Tests for moisture. The dish and dome method is used. An aluminum dish and dome (cover) is heated for 15 minutes, cooled in the desiccator and weighed. Approximately 5 grams of the sample is added to the dish, which is placed on the top of a water oven for 3 hours. After cooling in a desiccator for 20 minutes, the weight is taken. Loss in weight equals moisture present in original sample. A small quantity of T.N.T. sublimes but condenses on the inside of the cover, which should be cleaned thoroughly before using in another test.

T.N.T. extraction with benzene. A dry filter paper so folded as to leave a small cavity in the center is weighed in a tared weighing bottle. About 2 grams of powdered amatol is placed in the filter paper without removing it from the bottle, and the bottle is reweighed. The paper and amatol are transferred to a small funnel and washed with approximately 75 cc. of hot benzene, adding enough at a time to cover the powder. After about half the benzene has been added the remainder can be poured in rapidly, taking care to wash thoroughly the sides of the filter paper. The filter paper and residue are transferred from the funnel to the top of a steam oven in order to remove the greater portion of the benzene and dried in a tared weighing bottle for 1 hour. Loss in weight equals T.N.T. plus moisture.

Ammonium nitrate extraction with water. A known weight, approximately 2 grams, is extracted with 50 cc. of hot water at a temperature not less than 85°C. After cooling, the solution is filtered and the process repeated three times with successive quantities of hot water, 50 cc., 30 cc., and 20 cc. The combined filtrates are evaporated just to dryness in a tared dish, and left in a vacuum desiccator overnight. The residue is rinsed two or three times with anhydrous ether, dried on top of the oven to remove ether vapors, cooled, and weighed. The residue equals ammonium nitrate presnt in the sample.

Composition of amatol. Ammonium nitrate was first added to T.N.T. because the latter is a relatively expensive explosive. It had explosive properties and the mixture was cheaper on a weight basis.

T.N.T. has an oxygen deficiency where ammonium nitrate has an excess. It cannot reasonably be assumed that their reaction in a mixture is the same as individually.

T.N.T. has, because of its oxygen deficiency, some uncertainty in its action, but we may assume for it alone the explosion equation

$$C_7H_5(NO_2)_3 \rightleftharpoons 6\ CO + C + 2\tfrac{1}{2}\ H_2 + \tfrac{3}{2}\ N_2,$$

and for ammonium nitrate alone,

$$NH_4NO_3 \rightleftharpoons 2\ H_2O + N_2 + \tfrac{1}{2}\ O_2.$$

It may be supposed that in a mixture the oxygen excess will complete the oxidation of the T.N.T., and there are three possible and significant steps: (1) the oxidation of free carbon to carbon monoxide, (2) the oxidation of the hydrogen to water, and (3) the oxidation of the carbon monoxide to carbon dioxide. In 50–50 amatol there is more than enough ammonium nitrate for (1), and 80–20 corresponds approximately to (3).

TABLE 40

CHARACTERISTICS OF NH_4NO_3 — T.N.T. MIXTURES

Mixture		Property per kilogram		
T.N.T.	NH_4NO_3	n_1	Q_v	T_e, °C.
100	0	40.0	656	2,200
74	26	45.6	674 (1)	2,013
50	50	43.0	815	2,200
45	55	42.4	845 (2)	2,270
20	80	40.0	1,048 (3)	2,300
0	100	43.8	384	1,100

For these reactions the stoichiometrical relations are:

$$C_7H_5(NO_2)_3 + NH_4NO_3 \rightleftharpoons 7\ CO + 2\tfrac{1}{2}\ H_2 + 2\ H_2O + 2\tfrac{1}{2}\ N_2 \quad (1)$$

$$C_7H_5(NO_2)_3 + 3\tfrac{1}{2}\ NH_4NO_3 \rightleftharpoons 7\ CO + 9\tfrac{1}{2}\ H_2O + 5\ N_2 \quad (2)$$

$$C_7H_5(NO_2)_3 + 10\tfrac{1}{2}\ NH_4NO_3 \rightleftharpoons 7\ CO_2 + 23\tfrac{1}{2}\ H_2O + 12\ N_2 \quad (3)$$

By means of the equations and the usual calculations the results in Table 40 may be obtained.

From the standpoint of Q_v and maximum work, the 80–20 mixture would appear to be the best. Because of the lower velocity of explosion of ammonium nitrate there is a loss in *brisant* effect with increasing content, which is slight for 50–50 amatol, but greater for 80–20 amatol despite the high value for Q_v.

Picric Acid. Picric acid, 1:3:5 trinitrophenol, crystallizes in yellow leaflets, specific gravity 1.73, melting point 121.8°C., and explodes on heating. It is slightly soluble in cold water, more so in hot and soluble in alcohol. It is not hygroscopic. It is a direct yellow dye for silk, and stains the parts of the body with which it comes in contact. Externally it is not a poison and is a very good treatment for burns, but inhalation of the dust should be avoided.

Picric acid is acidic and forms salts readily. Many of the salts, known as picrates, are more sensitive explosives than picric acid, especially copper and lead, so it must in general be kept out of contact with metals. Potassium picrate is moderately insoluble in water. Its manufacture is a variation of the usual nitrating procedure.

Manufacture of Picric Acid.[6] Picric acid is made from benzene by two processes, known as the phenol and chlorbenzene processes.

Phenol process. Phenol is prepared from benzene as a raw material by first treating pure benzene with strong sulphuric acid and heating the mixture in jacketed iron kettles provided with agitation at a temperature of about 90°C. for several hours. The resulting benzene sulphonate is usually treated with lime, which converts it to calcium benzene sulphonate, which in turn is converted to sodium benzene sulphonate by means of sodium carbonate (soda ash). The sodium benzene sulphonate is dried and heated in fusion kettles with caustic soda, which converts it into sodium phenate. The fusion mixture is dissolved in water and treated with either carbon dioxide or sulphuric acid, which causes the phenol to separate out as a distinct layer. This layer is drawn off and distilled in order to separate the pure phenol from water and other impurities. Pure phenol is a white crystalline solid which melts at about 40°C.

For conversion to picric acid the phenol is melted into large jacketed iron kettles and treated with sulphuric acid of about 93% strength; the mixture is heated with stirring at a temperature of about 95°C. from 4 to 6 hours. The resulting phenol sulphonic acid is diluted with water and treated in a large acid-proof brick-lined nitrator with 42°B. nitric acid (about 70%). The reaction generates heat and the mixing is therefore carried on very slowly, the maximum temperature being about 110°C. After cooling the mixture, the crystallized picric acid is separated from the spent acid on a vacuum filter, washed with water, and dried.

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[6] U. S. A., TM 9–2900, *Military Explosives.*

Chlorbenzene process. Although this process has been quite extensively used abroad, its use in the United States until recently has been rather limited. Briefly, the process involves initial treatment of benzene with gaseous chlorine, whereby monochlorbenzene results. This product is purified by distillation and then nitrated with a mixture of nitric acid and sulphuric acids to give dinitrochlorbenzene. The latter, on treatment with lime or soda, loses its chlorine and becomes calcium or sodium dinitrophenolate, which on acidifying is converted to dinitrophenol. The dinitrophenol is readily nitrated to picric acid (trinitrophenol) by means of nitric and sulphuric acids.

Uses of Picric Acid. The fact already noted—that picric acid combines readily with some metals to form picrates which are unduly sensitive to friction, shock, or heat—has been a deterrent to the use of picric acid for military purposes in spite of the fact that it is a stronger explosive than T.N.T. The use of a nonmetallic lining for the shell cavity—for example, certain lacquers, varnishes, or paints,—obviates to a great degree the danger of formation of these salts. Introduction of T.N.T. as a military explosive has resulted in gradual abandonment of picric acid by practically every country except France, where it was largely used during the First World War. In the United States picric acid is used for conversion into "Explosive D" or ammonium picrate, which is used in base-fuzed shells for seacoast cannon and in all armor-piercing shells. Picric acid has also found use as a booster explosive and even as a substitute for part of the mercury fulminate charge in detonators.

Picric acid has been used extensively in the form of mixtures with other nitro compounds. Such mixtures, having a lower melting point than picric acid, can be melted and cast at temperatures below 100°C. The mixtures are more generally practical for use because of the hazard involved in melting picric acid at the relatively high temperature required. Some of the compounds which have been used with picric acid are trinitrotoluene, trinitrocresol, trinitrobenzene, and the di- and mononitro derivatives of phenol, cresol, and naphthalene. Little change in *brisance*, if any, results from the addition of the trinitro compounds, but the addition of the mono- and dinitro compounds causes a reduction in *brisance* in proportion to the amount added.

Inspection of Picric Acid. Chemical requirements[7] prescribed for picric acid by United States Army specifications are as follows:

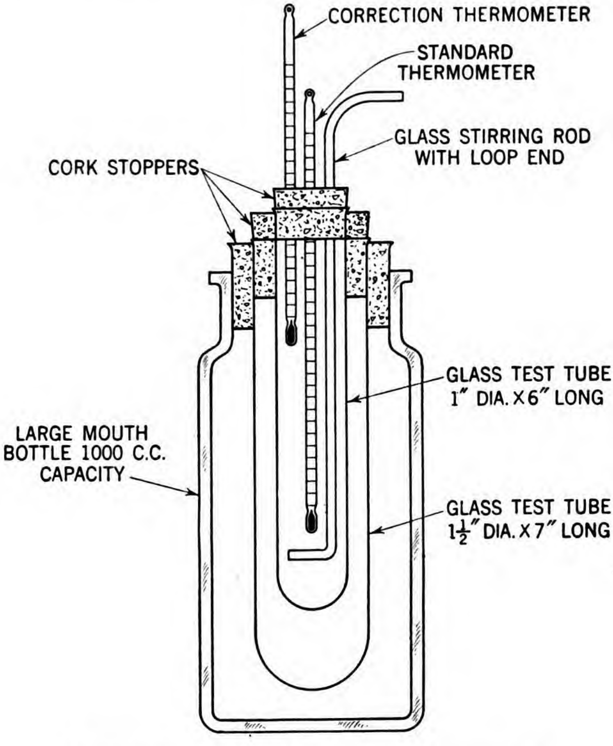
CORRECTION THERMOMETER
STANDARD THERMOMETER
GLASS STIRRING ROD WITH LOOP END
CORK STOPPERS
GLASS TEST TUBE 1″ DIA. X 6″ LONG
LARGE MOUTH BOTTLE 1000 C.C. CAPACITY
GLASS TEST TUBE 1½″ DIA. X 7″ LONG

FIGURE 36: **Solidification-Point Apparatus**

(1) It must have a solidification point of not less than 120°C. (2) It must contain: (*a*) Moisture, not more than 0.2% if purchased dry, and not more than 22% if purchased wet; (*b*) sulphuric acid, not more than 0.1%, both free and combined; (*c*) nitric acid, none free; (*d*) ash, not more than 0.2%; (*e*) material insoluble in water, not more than 0.2%; and (*f*) lead, not more than 0.0004%. (3) It must

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[7] U. S. A. Specifications 50–13–2A.

be of a white to yellow color. (4) Not less than 99.5% shall pass a No. 14 U.S. standard sieve.

Methods prescribed for testing picric acid are as follows:

Solidification point. A sample of the picric acid to be used for this test must be dried to constant weight at a temperature not exceeding 50°C. The apparatus used is illustrated in Figure 36. A test tube 1 inch in diameter and 6 inches long is fitted through a cork into a second test tube 1½ inches in diameter and 7 inches long, which in turn is set into a large-mouthed liter bottle. Into the inner tube is fitted a cork stopper through which are three openings. One is in the center, for the standard thermometer, which should be graduated in 0.1°C. One is immediately at the side of the center hole and is for a small thermometer which is passed just through the stopper; the reading of this is taken as the average temperature of the exposed stem of the standard thermometer in making the stem correction. The third hole in the stopper is a small V-shaped opening at the side through which passes a wire whose lower end is bent in a loop at right angles to the axis of the tube, for use as a stirrer. The inner test tube is removed and charged with approximately 50 grams of the sample. It is then placed in an oven at a temperature of 130°C. until the picric acid has attained the temperature of the bath throughout. The tube is then assembled in the apparatus for cooling, the standard thermometer immersed in the picric acid with its bulb in the center of the molten mass, and stirring continued vigorously as the temperature falls. The temperatures of both thermometers should be recorded every 15 seconds in order to note the extreme temperature reached on the slight rise of temperature which results during crystallization. This maximum temperature, corrected for emergent mercury column, is taken as the solidification point.

Moisture. A sample of about 5 grams of the picric acid is accurately weighed in a previously tared wide-mouthed weighing bottle at least 1½ inches in diameter, and dried for 5 hours or to constant weight in a drying oven at 70°C. The loss of weight is calculated as percentage of moisture in the original sample.

Sulphuric acid. A known weight of picric acid, approximately 10 grams, is dissolved in 250 cc. of boiling distilled water, acidulated with hydrochloric acid, and the solution is heated. A slight excess of hot solution of barium chloride is then added with constant stirring, the precipitate is allowed to settle, and the mixture is filtered while hot on a tared Gooch crucible. The latter is washed thoroughly with hot water, dried for 3 hours at 100°C., and the weight of $BaSO_4$ calculated as H_2SO_4 in the original sample.

Nitric acid. A water solution of picric acid is tested with a solution of diphenylamine in concentrated sulphuric acid. No coloration should result.

Ash. A known weight of picric acid, approximately 5 grams, is moistened with strong sulphuric acid in a tared crucible and carefully burned until all carbonaceous residue has been eliminated. To compensate for reduction of metallic salts, a few drops of nitric acid and sulphuric acid are added and carefully evaporated; the crucible is again ignited, cooled in a desiccator, and weighed.

Insoluble material. About 10 grams of the sample is dissolved in 150 cc. of boiling water, boiling continued for 10 minutes. The solution is filtered while hot through a tared Gooch crucible, which is washed thoroughly with hot water and dried for 2 hours at 100°C.

Lead. A known weight, approximately 300 grams of the picric acid, is placed in a 2-liter flask and allowed to soak in 100 cc. of a hot saturated solution of barium hydroxide in 65% alcohol. The flask is well shaken, 1,400 cc. of 95% alcohol is added, and the whole is allowed to digest at a temperature below the boiling point of alcohol until all the picric acid has been dissolved with the exception of small particles of insoluble matter. The solution is shaken thoroughly and allowed to stand in the cold until most of the picric acid has crystallized out; then it is filtered. It is not necessary to disturb the crystalline picric acid at the bottom of the flask, as only 500 cc. of the solution is used for completion of the tests and this amount can be decanted. To 500 cc. of this filtered solution, which represents 100 grams of picric acid, four or five drops of nitric acid and 10 cc. of a 1% mercuric chloride solution are added and a slow stream of hydrogen sulphide is passed through this solution for 15 minutes. After allowing it to settle 20 minutes, the solution is filtered and the precipitate is washed with alcohol saturated with hydrogen sulphide; the filter paper is dried and ignited in a porcelain crucible; 9 cc. of nitric acid, specific gravity 1.42, is added and the solution is warmed on a hot plate. Enough warm water is then added to make up the volume to 50 cc. The solution is electrolyzed with a current of 0.4 ampere and

2½ volts at a temperature of 65°C., using a tared platinum anode. After 1 hour, the electrode is washed by replacing the beaker with another one full of distilled water without interrupting the current. The tared anode is dried and weighed. The weight of lead peroxide, found by difference, multiplied by 0.8661, gives the percentage of lead.

Granulation. A weighed portion of 50 grams of the sample is placed on a No. 14 U.S. standard sieve to which a bottom pan has been attached. Two metal washers are placed on the sieve and shaken for a maximum of 3 minutes, or until no more material passes through the sieve. Any material remaining on the sieve is weighed and the percentage passing through the sieve is calculated.

Picric Acid as an Explosive. Picric acid as an explosive has about the same sensitivity to shock or friction as T.N.T., but is more readily detonated, and is a more powerful explosive. Q_v (probably high) is 810 Calories per kilogram, T_e is 2,430°C., and the Trautzl-block expansion is 305 cc. (10 grams) as recorded. Picric acid may have a detonation velocity of 7,000 meters per second. The explosion reaction may be

$$2\ C_6H_3N_3O_7 \rightleftharpoons 3\ N_2 + 12\ CO + 2\ H_2O + H_2,$$

but it yields a black smoke.

It has been extensively used as a military bursting explosive abroad under various names—lyddite, melinite, shimose—both alone and mixed with such other explosives as T.N.T. and T.N.X., and some mixtures can be loaded by pouring. It is not used much now in the United States. Tridite is 80% picric acid, 20% dinitrophenol, melts at 90°C., and can be loaded by pouring.

Ammonium Picrate. This is the ammonium salt of picric acid. Its use as an explosive is credited to Nobel, by patent, although it had been used before. In the United States it is known as Dunnite or Explosive D. It crystallizes from hot water in yellow-red rhombic needles with a specific gravity of 1.719, decomposing on melting, and exploding at 300° to 423°C. It can react with metals like picric acid, but unless wet the action is slight.

As an explosive, ammonium picrate is marked by great insensitivity, is used for that reason in armor piercing shells, and is the least sensitive of all the military high explosives. The explosion reaction yields some free carbon, but less smoke than picric acid. Q_v is 622, T_e = 2,000°C., lead-block expansion (10 grams) is 275 cc., velocity of detonation is about 7,000 meters per second (but below this probably) as recorded. It is hygroscopic and water reduces its strength and sensitivity. It should be stored in wooden containers or kept in glass in the laboratory, not metal.

Manufacture of Ammonium Picrate.[8] This consists in the main of a simple neutralization of picric acid by means of ammonia, either alone or in combination with ammonium carbonate. This process is not attended with any serious manufacturing difficulties or dangers, provided the possibility of leaking ammonia pipes is excluded.

Details of manufacture are as follows: Approximately 300 pounds of picric acid are mixed with 500 gallons of water at room temperature and then slowly heated by direct steam. As the mixture warms, aqua ammonia is added at the bottom of the tank until neutralization is completed. In some factories it was the practice to add a faint excess, thus insuring complete neutralization of all the picric acid, this condition being evidenced by the formation of a reddish colored crystalline mass of ammonium picrate. United States Army specifications permit a maximum of .025% acidity or alkalinity. When this stage has been reached the resulting material is dropped into tanks for crystallization. These tanks are so equipped that a continual agitation of their contents can be maintained by air with the object of accelerating the crystallizing of the ammonium picrate during the cooling. When the mass has cooled to about 25°C. the crystals are separated from the mother liquor by filtering or draining. From the crystallizing tank the ammonium picrate is taken to the dry house, where it is subjected to a temperature of about 45°C. for 8 hours in drying bins which are so constructed that warm air circulates constantly through the mass. Finally the dried material is screened by means of a rotating screen and sent directly to the packing room. The finished product is then packed in 50-pound boxes lined with waterproof paper and sent to storage.

Reworking ammonium picrate consists in redissolving impure or waste ammonium picrate in water, removing the impurities by filtration, then heating the solution by steam coils until it has been evaporated sufficiently to produce crystallization. From here on the reworking operations are exactly the same as those followed out in the manufacture of the new material.

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[8] U. S. A., TM 9–2900, *Military Explosives.*

Uses of Ammonium Picrate. This explosive is used as the bursting charge for armor piercing shells on account of its insensitiveness to shock, which permits a shell to pass through armor without exploding. Owing to the fact that it cannot be melted without decomposing, it must be loaded into the shell by pressing. The interior of the shell is covered with a suitable nonmetallic paint or varnish. It has no commercial use as an explosive, although it enters into the composition of numerous patented blasting explosives which have not been used to any great extent.

Inspection of Ammonium Picrate. United States Army specifications[9] prescribe the following requirements for ammonium picrate: (1) ammoniacal nitrogen, not less than 5.64%; (2) moisture, not more than 0.2%; (3) solubility, not more than 0.2% insoluble; (4) ash, not more than 0.2%; (5) acidity or alkalinity, not more than 0.025%; (6) color, yellow to red; (7) granulation—(*a*) through No. 14 U.S. standard sieve, 99.5% minimum; (*b*) through No. 100 U.S. standard sieve, 20% maximum.

Tests and determinations covering each of the listed criteria are made on ammonium picrate to determine its suitability for military use.

Ammoniacal nitrogen. A known weight of the ammonium picrate to be analyzed, approximately 1 gram is placed in a 500-cc. Kjeldahl flask (see Figure 37). The flask is equipped with a two-hole rubber stopper which carries an exit tube leading away to a bottle containing $N/10$ sulphuric acid, and an ingress tube reaching to its bottom, through which air that has already been dried and freed from ammonia by passage through concentrated sulphuric acid may be bubbled. Twenty cubic centimeters of water is introduced into the flask, 12 cc. of 5% sodium carbonate solution is added, the flask is set in a boiling water bath, and ammonia-free air is bubbled through until contents of the flask have been evaporated to dryness. The ammonia is absorbed by bubbling the air through 50 cc. of $N/10$ sulphuric acid, a bulb full of very small holes, such as may be made conveniently with a hot platinum wire, being used for the purpose. To deal with the possibility of splashing of the sulphuric acid, the exit tube from the bottle is equipped with a trap. The excess sulphuric acid is titrated with $N/10$ sodium hydroxide, using methyl red or sodium alizarin sulphonate as an indicator, the amount which has been consumed is noted, and the ammoniacal nitrogen in the sample is calculated by the formula:

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[9] U. S. A. Specifications 50–13–3C.

$$\text{percentage of ammoniacal nitrogen} = \frac{1.401\,(AB - CD)}{E},$$

where A = the number of cubic centimeters of sulphuric acid solution in the bottle, B = normality of the sulphuric acid solution, C = the number of cubic centimeters of sodium hydroxide solution used, D = normality of sodium hydroxide solution, and E = weight of sample.

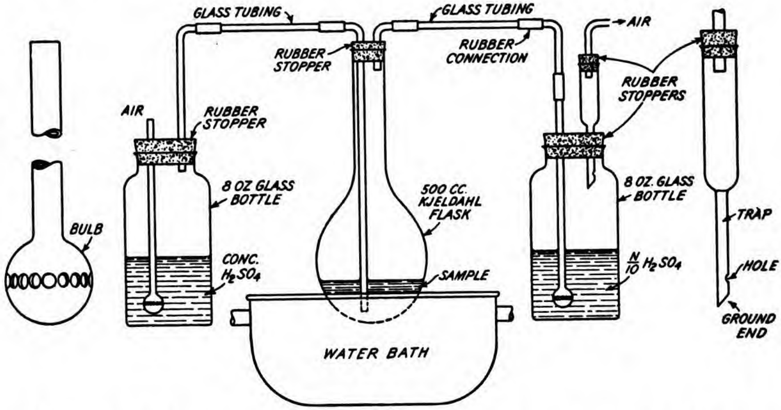


FIGURE 37: **Apparatus for the Determination of Ammoniacal Nitrogen in Ammonium Picrate**

Moisture. A sample of about 5 grams of the ammonium picrate is accurately weighed in a previously tared wide-mouthed weighing bottle at least 1½ inches in diameter and dried for 2 hours or to constant weight in a drying oven at 100°C. The loss of weight is calculated as percentage of moisture in the original sample.

Insoluble material. A known weight, approximately 10 grams, is dissolved in 150 cc. of hot distilled water by boiling for 10 minutes. The solution is filtered through a tared Gooch filter, the insoluble residue washed thoroughly with hot water, and dried for 1 hour at 100°C.

Mineral matter (ash). A known weight, approximately 2 grams, is wetted with molten paraffin in a tared crucible and carefully burned until all carbonaceous residue has been eliminated. It is cooled in a desiccator and weighed.

Acidity or alkalinity. A representative sample of 5 grams of the ammonium picrate is ground in a porcelain mortar with 50 cc. of water at room temperature, and the supernatant liquid is poured through a folded filter, the filtrate being caught in a 500-cc. Erlenmeyer flask. This process is repeated until all of the ammonium picrate is brought into solution and the total volume of the filtrate is 250 cc. Three drops of sodium alizarin sulphonate or a 1% alcohol solution of methyl red indicator are added. The solution is shown to be acid if either of the indicators assumes a yellow color. If the solution is acid, it is titrated with approximately $0.1N$ sodium hydroxide solution and the percentage of picric acid in the sample is calculated according to the formula

$$\text{percentage of picric acid} = \frac{22.905\,AB}{C},$$

in which A = the number of cubic centimeters of sodium hydroxide solution used, B = the normality of the sodium hydroxide solution, and C = the weight of the sample. If the solution is shown to be alkaline by the indicator assuming a purple or red color, it is titrated with approximately $0.1N$ sulphuric or hydrochloric acid. The percentage of free ammonia in the sample is calculated according to the formula

$$\text{percentage of free ammonia} = \frac{1.7034\,AB}{C},$$

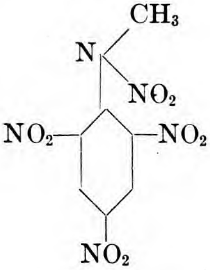
in which A = the number of cubic centimeters of acid solution used, B = the normality of the acid solution, and C = the weight of the sample.

Granulation. A No. 14 U.S. standard sieve is fitted on a No. 100 U.S. standard sieve and a receiving pan attached to the bottom sieve. A weighed portion of 100 grams of the sample and two metal washers are placed on the upper sieve, covered, and shaken 3 minutes. The material retained on the No. 14 sieve and that passing through the No. 100 sieve are weighed and each weight is calculated as a percentage of the whole sample.

Storage of Ammonium Picrate. Storage is governed by the same regulations applicable for the storage of T.N.T., both as to type of magazine and rules for handling, and special regulations governing this particular explosive are not necessary.

Ammonium picrate which has been pressed at a shell-loading plant and removed from a shell is very much more sensitive to shock or blow than new material, and there are cases on record where serious accidents have happened in the loading of shells with ammonium picrate so treated. If it becomes necessary to store this material, special precautions should be observed to protect it against shock or fire, and it should preferably be stored in a building by itself.

Although less sensitive than T.N.T., ammonium picrate can be exploded by severe shock or friction, is highly inflammable, and when heated to a high temperature may detonate. It is therefore necessary that it be treated with proper care as a high explosive.



Tetryl

Tetryl. Tetryl, more properly called trinitrophenylmethyl nitramine, is a very important explosive widely used as a booster, and as a priming charge in addition to fulminate in blasting caps. The prue compound forms yellow crystals, specific gravity 1.6, melting point 130°C., exploding at 187° to 260°C., very slightly soluble in water, but soluble in alcohol and ether. It is toxic and not hygroscopic. Its manufacture properly begins with dimethylaniline, which also nitrates too readily to be treated in the usual way.

As an explosive tetryl is more sensitive to shock than the compounds already described. It frequently explodes with a drop of only 20 centimeters of the 2-kilogram weight but usually runs just below them in sensitivity and above 50 centimeters. The explosion equation may be

$$2\ C_7H_5N_5O_8 \rightleftharpoons 14\ CO + 3\ H_2 + 2\ H_2O + 5\ N_2.$$

T_e is 2,911° to 3,339°C., Q_v = 908 Calories per kilogram, and lead-block expansion is 320 cubic centimeters (10 grams). (These are recorded values. On theoretic grounds tetryl might be expected to approximate nitroglycerine. Calculate and compare.) It is more readily detonated than T.N.T. It has a high velocity, 7,229 meters per second, which is the principal reason for its use as a booster, and it explodes by a rifle-bullet impact. It is a definitely toxic material producing anemia and skin eruptions in many workers.

Manufacture of Tetryl.[10] Dimethylaniline is dissolved in a large excess of 96% sulphuric acid. This solution is added to nitric acid or (usually) to a mixture of nitric and sulphuric acid such that nitric acid represents about 30% of the final mix, in a nitrator provided with cooling and agitation. The temperature is kept from 68° to 72°C. (This procedure may be used as the basis for a laboratory method.)

The tetryl is separated from the acid by filtration or by drowning in water and separation. Then the tetryl is given short boiling treatments to reduce the acidity to 0.5% or less. The excess water is removed by filtration and the crude tetryl is purified by crystallization from benzene, acetone, or nitric acid. In recrystallizing, conditions are controlled so that the granulated finished product is free-flowing, to meet the requirements for the manufacture of tetryl pellets in automatic processes.

Inspection of Tetryl.[11] Detailed requirements specify: (1) color, light yellow or buff; (2) melting point, minimum 128.75°C.; (3) granulation, (*a*) through No. 12 U.S. standard sieve, minimum 100%, (*b*) through No. 16 U.S. standard sieve, minimum 95%, (*c*) through No. 100 U.S. standard sieve, minimum 20%; (4) moisture, maximum 0.10%; (5) insoluble matter, maximum 0.10%; (6) acidity, maximum 0.03%; (7) grit, none. Maximum lot is 50,000 pounds.

Sampling is done as follows: Select a minimum of 10 boxes of packed tetryl, or at least 1 box for every 5,000 pounds, so as to be representative of the lot. Sample each selected box by removing from different parts of the box enough of the material to give a primary sample of about 1 pound. Mix this sample thoroughly, and place a 4-ounce portion in a bottle so labeled that the box from which the sample was taken can be easily identified. The remainder of each primary sample should weigh about 12 ounces. Mix these remainders thoroughly and quarter until a composite sample of about 1 pound is obtained. Place the composite sample in a rubber-stoppered bottle and label this so as to show the name of the material, manufacturer, plant, purchase order, and the number of pounds in the lot. All acceptance tests are made on the composite sample representative of the lot. Hold the primary samples for possible future examination should the composite sample fail to meet the requirements.

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[10] For a laboratory method see Tenney Davis, *Chemistry of Powder and Explosives*, p. 177.

[11] U. S. A. Specifications 50–13–4C.

Melting point. Set up a melting-point bath equipped with a mechanical stirrer and a source of heat that can be easily regulated. A beaker of 1 or 2 liters capacity about three-quarters full of clean paraffin oil is recommended. Suspend an accurately standardized thermometer in the bath so that the bulb is not less than 1½ inches from the bottom of the bath; if the mercury column will not be completely immersed at the temperature of the observed melting point, suspend a second thermometer at about ½ inch from, and with its bulb about the height of the middle of the exposed mercury column of the first thermometer.

Grind a small portion (not over 5 grams) of the sample so that it will pass a 100-mesh sieve, and dry it for 2 hours at 100°C. or over sulphuric acid in a desiccator for 48 hours. Use thin-walled capillary tubes of uniform diameter, long enough to extend to the top of the bath. Fill the tube with ground tetryl to a depth of approximately 4 millimeters, compact by tapping, and fasten the tube of the standardized thermometer so that the lower end of the tube is in contact with the bulb of the thermometer. Start the stirrer and heat the bath rapidly to about 120°C., then gradually so that the rise in temperature does not exceed 1° in 3 minutes. Record the temperature observed at the instant the meniscus of melted tetryl first appears across the capillary tube.

If the mercury column is completely immersed at the above temperature, report this temperature as the melting point of the sample. If part of the column is exposed, add the following correction to the observed melting point:

$$n(T - t) \times 0.000159.$$

In this computation, n = the number of degrees in the exposed column; T = the uncorrected melting point; t = the average temperature of exposed column, that is, temperature indicated by a second thermometer; and 0.000159 = coefficient of expansion of mercury in glass.

Granulation. Assemble a nest of U. S. standard sieves Nos. 12, 16, and 100, and fit on a pan. Place 100 grams of the sample on the upper sieve. Cover and shake for 3 minutes. Weigh the material held on and calculate the percentage passing through each sieve.

Moisture. Weigh accurately a sample of about 5 grams in a tared weighing dish of at least $1\frac{1}{2}$ inches diameter, and dry for 2 hours at 100°C., or over sulphuric acid in a desiccator for 48 hours. Calculate the loss in weight as the percentage of moisture.

Insoluble matter. Dissolve a known weight of about 5 grams of the sample in 75 cc. of benzene by heating to about 75°C. and stirring. Cool the solution to room temperature and filter it through a tared Gooch crucible; wash the residue with three 25-cc. portions of benzene, dry to constant weight at 100°C., and calculate the percentage of insoluble matter.

Acidity. Dissolve a weighed portion of approximately 5 grams of the sample in 150 cc. of benzene. Transfer the solution to a separatory funnel and shake with 100 cc. of cold, recently boiled distilled water. Allow the liquids to separate, draw off the water, and wash the benzene solution with another 50 cc. of cold boiled water. Titrate the combined water washes with approximately $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. Calculate the acidity as percentage of sulphuric acid.

Grit. Transfer a 50-gram portion of the sample to a beaker and dissolve in 100 cc. of acetone. Pour the solution through a No. 60 U.S. standard sieve and wash any residue on the sieve with a jet of acetone from a wash bottle. When no more insoluble material passes through the sieve, dry the sieve and the residue remaining on it. Transfer the dry residue to a piece of paper and then to a smooth glass slide. Rub the material on the glass by exerting pressure with a smooth steel spatula blade. Note if particles of grit are present as indicated by lack of uniformity of the material and the persistence of a scratching noise when pressing and rubbing of the material on the glass is continued.

Packing. Tetryl is packed in rectangular boxes or fiber drums of 50 to 100 pounds capacity, lined with strong paraffined paper and so constructed as to comply in all respects with the requirements of the Interstate Commerce Commission regulations.

A *brisance* test was formerly prescribed for tetryl by the sand bomb (see page 377). The nitrometer nitrogen method determines one-fourth of the nitrogen.

Summary of the Nitro Compounds. Mononitrobenzene is readily prepared from benzene, and from it dinitrobenzene. Trinitrobenzene can then be made in poor yields with very large excess of acid by heating at 100°C. for a long time. Trinitrobenzene is more readily prepared by oxidizing T.N.T. in sulphuric acid with chromic oxide. T.N.B. is less sensitive and more powerful than T.N.T. and has a higher velocity of explosion.

Dinitrochlorbenzene and even trinitrochlorbenzene can be prepared by direct nitration, and have some interest. They are powerful explosives which yield phosgene on explosion.

Commercial xylenes are a mixture which is separated by a chemical process to yield metaxylene, which may then be somewhat more easily nitrated to yield a trinitrometaxylene, T.N.X., which has some application.

Explosives more highly nitrated than the tri derivatives of benzene, toluene and xylene can be made with difficulty, but although powerful, they are not used.

Explosives result from nitration of naphthalene; diphenyl and triphenyl; phenols such as cresol and resorcincol; aniline, and a variety of related more complex compounds. Many of these have had minor uses in explosive mixtures; cheddite, for instance, contains nitronaphthalenes and a chlorate. Many homologues of tetryl have been made, of which pentryl (trinitrophenyl-nitramine-ethyl-nitrate), more powerful than tetryl, is the most significant. (See Table 41.)

T.N.T. nevertheless remains as the outstanding military explosive of this group, on a weight basis. This is an over-all evaluation of its characteristics since no single one would ordinarily account for that.

Among its advantages may be included cheapness as compared with other nitro derivatives, ease of manufacture, power, ease of loading by pouring due to low melting point, insensitivity, and stability in keeping and in contact with other materials. Among its disadvantages may be listed cost, which does not enable it to compete with the commercial explosives; difficulty of manufacture, also greater than most commercial explosives; sensitivity, greater, and power, less, than some of the other nitro derivatives; and a very large oxygen deficiency.

These considerations indicate some of the reasons for the employment of the other nitro derivatives, as well as fields for further improvement. Tetranitroaniline, T.N.A. (2:3:4:6), is easier to make, and is a more powerful explosive but more sensitive and reactive. The development of processes for the production of toluene by the cracking of petroleum since the First World War has made T.N.T. cheaper under war conditions than it formerly was.

Picric acid is more powerful than T.N.T. but is much more reactive, in contact with metals particularly. Tetryl is considerably more powerful than T.N.T. but is also more sensitive. Its high velocity of detonation makes it suitable as a booster. Ammonium picrate is less powerful than T.N.T. but is also less sensitive. Homologues of tetryl have been tested and are similar to it. Nitro derivatives of naphthalene and the higher condensed cyclic hydrocarbons in general are less powerful explosives than T.N.T. except at impractically high nitrations. Nitro derivatives of the polyphenyls compare favorably, as well as of the polyphenols and phenol esters, but are expensive. This statement includes diphenylamine and benzidine derivatives. These compounds have indicated applications only where an exceptional characteristic warrants a specific use, even though some of them have higher power than T.N.T.

Gaseous Explosives. Before concluding a survey of explosive materials, some mention should be made of gaseous explosives, although they are in no way chemically related to those just discussed. If this text were written from a theoretical standpoint, it would be necessary to devote a considerable part of the volume to them. And practically, in the field of power generation by the internal-combustion engine, they might be considered even more important than those presented, but we have limited ourselves to the specialized commercial and military uses of explosives.

Explosive single gases are known, for example ClN_3, ClO_2, and C_2H_2, which explode into their constituents, but these are of little practical use or importance, except as the cause of accidents on occasion. Any combustible gas may yield an explosive mixture when mixed with oxygen or air, if the resulting reaction results in a volume

TABLE 41

MISCELLANEOUS NITRO COMPOUNDS

Name	Formula	Molecular weight	Melting point, °C.	Notes
Trinitroresorcinol	$C_6H(OH)_2(NO_2)_3$	245	180	weaker than picric acid
Trinitrocresol	$CH_3C_6H(OH)(NO_2)_3$	243	106	weaker than picric acid
Tetranitroaniline	$C_6H(NH_2)(NO_2)_4$	227	210	similar to tetryl
Ethyl tetryl	$C_6H_2(NO_2)_4N \cdot C_2H_5$	301	96	similar to tetryl
Trinitroxylene	$C_6H(CH_3)_2(NO_2)_3$	241	182	much weaker than T.N.T.
Hexanitro-diphenyl	$C_{12}H_4(NO_2)_6$	424	236	powerful
Trinitronaphthalenes	$C_{10}H_5(NO_2)_3$	263	110	much weaker than T.N.T.
Hexanitrodiphenylamine	$(C_6H_2)_2NH(NO_2)_6$	439	245	powerful

increase and particularly if it is exothermic. The mixture does not have to be a true gas, but may be a colloid suspension; coal dust and flour, are the sources of serious industrial explosions, and any organic dust may be. The explosive system thus set up is subject to the same considerations which govern in the cases we have examined, except that the behavior of the homogeneous and simple ones, as hydrogen and chlorine, is capable today of more exact analysis. Such studies have yielded very important information, and have thrown much light on the exact chemical mechanism of many of the reactions.

TABLE 42

EXPLOSION LIMITS IN AIR

Gas	Volume per cent	
	Minimum	Maximum
H_2	9.55	66.5
CO	16.50	75.0
Water gas	12.50	66.5
Methane	6.00	13.0
Acetylene	3.50	52.5
Pentane	2.50	4.8

The ideal explosion mixture for such systems may be calculated from the equation, for example,

$$H_2 + Cl_2 \rightleftarrows 2\ HCl,$$

where the ideal composition would be 50% + 50% by volume. Ideal composition for air may be roughly computed on the assumption that air is one-fifth oxygen. In practice, in such cases, it is found that any mixture within what is sometimes called the explosion limits will explode under proper conditions, and these limits vary widely, as is shown in Table 42. The limits are to some extent dependent upon conditions. Practically, however, this latitude in the explosion limits means that the handling of volatile inflammable liquids in quantity, especially in filling tanks where large volumes of nearly saturated vapor are driven from the tanks as the liquid fills them, is a hazardous undertaking, which must be surrounded with such proper safeguards as venting. Numerous and recurring explosions in gasoline filling stations, tankers, and the like testify eloquently to this. The extruded vapor can render explosive a relatively tremendous remaining open, and the mercury reservoir adjusted just low enough to give a slightly reduced pressure in the generating bulb. The generating bulb is shaken gently, keeping the lower end in a fixed position until most of the gas has been generated. The mercury reservoir is adjusted so that the mercury in the generating bulb drops nearly to the lower shoulder, whereupon the lower stopcock is closed and the bulb is shaken vigorously for 3 minutes. The bulb is replaced on the rack with the lower stopcock open and the mercury reservoir adjusted until the mercury in the generating bulb is at approximately the same height as the mercury in the reservoir. This adjustment is for the purpose of bringing the pressure inside of the generating bulb to approximately one atmosphere so that the solubility of the nitric oxide gas in the sulphuric acid will not vary too widely. The lower stopcock is closed and the bulb shaken vigorously for an additional 3 minutes. The gas is now transferred to the measuring tube and the levels of the mercury in the compensating tube and the measuring tube are adjusted to approximately the same height. The gas is allowed to stand for about 20 minutes in order to permit equalization of temperature of the gas in the two tubes, and the mercury levels closely adjusted with a leveling device. The reading of the measuring tube is divided by the weight of the sample of nitrocellulose, giving the percentage of nitrogen in the nitrocellulose. The tare weight of the weighing bottle may be obtained before or after the test.

Ash. Two grams of dried nitrocellulose are placed in a recently ignited and tared crucible and treated with sufficient acetone containing 5% castor oil (by volume) to gelatinize it thoroughly. The nitrocellulose is then ignited and allowed to burn without applying heat until a charred residue remains, and finally it is thoroughly ignited, cooled, and weighed; the percentage of ash is then calculated. If preferred, the nitrocellulose may be digested with nitric acid, ignited carefully, and the ash determined.

Testing Smokeless Powder.[4] *Ballistic samples.* The number of containers required to make up the ballistic sample and the chemical and stability sample should be selected so as to be representative of the lot. If the weight of the samples required is less than 10 containers, a portion equal to one-tenth the weight of the required ballistic sample should be removed from each of 10 boxes and those 10 portions should be packed in individual airtight containers. It is desirable that the ballistic sample be taken not sooner than two weeks after the original packing.

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[4] See U. S. A. Specifications 50–12–3A, 50–12–5, 50–12–11A.

Chemical and stability samples. From each of the containers sampled for the ballistic tests, equal portions of the powder should be removed so as to have a sample for the chemical and stability tests of approximately the weight desired. Not less than 5 pounds of this sample should be set aside for 65.5°C. surveillance tests. The greatest cleanliness should be observed in handling the chemical and stability sample; handling it with damp or soiled hands should be avoided. The sample should be mixed thoroughly.

External moisture, air-dried. A sample of about 20 grams of the powder (or two whole grains, if a grain weighs more than 10 grams) is weighed accurately in a tared glass weighing bottle. It is dried in a vacuum oven (vacuum of at least 25 inches of mercury) at 55° ± 2°C. for 6 hours, cooled in a desiccator, and weighed. The loss in weight is calculated as the percentage of moisture in the sample.

External moisture, water-dried. A powder sample of about 20 grams (or two whole grains if a grain weighs more than 10 grams) is weighed accurately in a tared glass weighing bottle. It is dried for 6 hours at 100 ± 2°C. at atmospheric pressure, cooled in a desiccator, and weighed. The loss in weight is calculated as the percentage of moisture in the sample.

Diphenylamine. A sample of 5 grams of the powder is weighed accurately into a 250-cc. lipped beaker. The sample may be in whole grains if small enough to give a fair sample or in slices of medium or larger grains. Ten cubic centimeters of glacial acetic acid and twenty cubic centimeters of nitric acid (specific gravity 1.42) are mixed and poured on the powder. The beaker is covered with a watch glass and placed on a steam bath at about 95°C. for 1½ hours. It is necessary that the above quantities of acid be strictly adhered to by using either a pipette or graduate for the measurement. The powder dissolves completely with copious evolution of red fumes. The time and temperature given allows all red fumes to be dissipated without too much reduction of volume, and this is the end to be attained, since the nitro compounds have a tendency to crystallize out if the solution is evaporated too much or is allowed to stand too long after removal from the steam bath. Whenever such crystallization occurs results are slightly low.

Immediately after heating on the steam bath is completed, the solution is cooled, care being observed not to agitate, and poured into 75 cc. of distilled water which has been cooled to 15°C. in a 250-cc. glass-stoppered Erlenmeyer flask. The beaker is washed with water so that the solution, including washings, will be approximately 120 cc. The flask is shaken well for about 2 minutes and allowed to stand overnight.

The nitro compound is filtered on a Gooch crucible prepared by washing with 10% nitric acid and igniting. The nitro compound is washed six or seven times with water containing 1% of nitric acid, dried at 100° to 105°C. for 1 hour, cooled in a desiccator, and weighed. The crucible is placed in a small beaker, 10 cc. of acetone added, and allowed to soak for 15 minutes. The crucible is placed on a suction flask and washed with small quantities of acetone until nitro compounds are completely removed. The crucible is dried at 100° to 105°C. for 1 hour, cooled in a desiccator, and weighed. The loss in weight is calculated as the quantity of nitro compounds.

The factor for conversion of nitro compounds to diphenylamine, using the quantities of acid stated above, is 0.4259.

$$\%\text{ of diphenylamine} = \frac{\text{weight of nitro compound} \times 0.4259 \times 100}{\text{weight of powder}}$$

Graphite. The crucible used for the determination of diphenylamine is placed in a muffle furnace or in an inclined position over a gas burner and heated strongly until all carbonaceous material has disappeared. The crucible is cooled in a desiccator and weighed. The loss in weight is calculated as the percentage of graphite in the sample.

Total volatiles. The volatile determination is started as soon after receipt of the sample as possible. Any grains which have been handled should not be returned to the sample, except in special cases where the sample available is very small. The sample container is kept tightly closed. About 20 grains of all powders are used, regardless of caliber. A total of at least 2 grams is cut, taking approximately the same number of slices from each grain, after first cutting off and discarding about ¼ of the grain so that the slices used come from approximately midway between end and center of the grain. Each slice is cut so as to have as nearly as possible the same thickness at all parts of its area. The slices are cut either clear across the grain, giving a circular area, or just half across, giving a semicircular area. A sample of about 1 gram is weighed accurately into a tared aluminum can, approximately 50 millimeters high and 90 millimeters in diameter, provided with a tight-fitting lid and an aluminum stirring rod, the weight of which is included in the weight of the can. This sample is treated with 50 cc. of alcohol complying with United States Army Specification 4–10-18, and 100 cc. of ether complying with United States Army Specification 50–11–45. This mixture should be stirred frequently if it is desired to hasten solution, or the can should be covered and left under a bell jar overnight. When solution is complete the ether that has evaporated is replaced. The can is placed on a steam box or on a closed steam bath and a portion of the ether evaporated. The aluminum can should not be permitted to come in contact with steam or hot water. The amount of ether evaporated before the precipitation of the nitrocellulose determines the character of the precipitate; if too much ether is evaporated the precipitate will be gummy and difficult to dry; if too little ether is evaporated the precipitate will be sandy and cause bumping. The amount of ether to evaporate in order to obtain the desired fine, flaky precipitate depends upon the amount of nitrocellulose present and can be learned only by practice. When it is considered that the correct amount of ether has been evaporated, 10 cc. of distilled water is added. If the solution becomes opaque, indicating that the precipitation has started, water is added slowly with constant stirring to make a total of 50 cc. If the 10-cc. portion of water does not start the precipitation, a little more ether is evaporated and again 10 cc. of water is added. This process is repeated until a 10-cc. portion of water starts the precipitation and the precipitation is finished by adding sufficient water to make a total of 50 cc. If the precipitate seems too heavy, 5-cc. portions of ether are added and stirred until the precipitate becomes light and flaky. The ether is evaporated with constant stirring until there is no further danger of bumping, and then just to dryness. The can is transferred to an oven at 95° to 100°C. and the precipitate is further dried for 1½ hours, cooled in a desiccator, and weighed. If the latter weighing does not check the former within 0.0005 gram, the $\frac{1}{2}$-hour dryings in the oven are repeated until the results check within this limit. A determination of nonvolatile residue at 95° to 100°C. is made on the quantities of water, alcohol, and ether used and the percentage of total volatiles is calculated as follows:

$$\text{percentage of total volatiles} = \frac{(A - B + C - D \times 100)}{E}$$

where A = original weight of can and sample; B = final weight of can and sample; C = weight of water, ether, and alcohol residues; D = correction in grams for volatilization of diphenylamine during the determination (25% of the diphenylamine content of the powder is allowed); and E = original weight of sample. The percentage of total volatiles, graphite, and diphenylamine is subtracted from 100 and reported as percentage of nitrocellulose in the sample.

Ash. From the remainder of the slices or grains a sample of about 1 gram is weighed accurately in a tared porcelain crucible. The sample is moistened with a small quantity of concentrated nitric acid and digested for 2 to 3 hours on a steam bath. The crucible is removed from the steam bath and heated over a Bunsen burner, cautiously at first to avoid loss. The crucible is finally placed in a muffle furnace, or over a gas burner, in an inclined position and partially covered with a lid, and heated strongly until all carbonaceous matter has disappeared; then it is cooled in a desiccator and weighed. From this weight the original weight of the crucible is subtracted and the result is calculated as the percentage of ash in the sample.

Compressibility. In this test, grains which are abnormal in shape or contain obvious flaws are not used. The ends of 10 normal grains of powder are cut so that new surfaces perpendicular to the length are exposed, and the length is equal to the diameter. The average length of these pieces is determined with a micrometer. Each grain is compressed between parallel surfaces, increasing the load slowly until the first crack appears. The load is removed and the grain is measured. The average reduction in length is calculated as a percentage of the average original length. If these 10 grains fail to pass this test, 20 more grains are subjected to the test. The average reduction in length is calculated in percentage of the average original length of the total 30 grains tested. This test is more completely described on page 129.

Heat test[5] *at 134.5°C.* Tests are made on five samples thus: 2.5 grams of sample are weighed out and each sample is placed in a test tube made of heavy glass, preferably pyrex, approximately 15 millimeters in inside diameter and 18 millimeters in outside diameter, and 290 millimeters long. Each sample should consist of grains as nearly whole as is consistent with a weight of 2.5 grams of sample. In sectioning grains to obtain the required weight, the grains are split longitudinally. A piece of standard normal methyl violet paper, 70 millimeters long and 20 millimeters wide is placed vertically in each tube, its lower edge 25 millimeters above the powder. The tubes are stoppered with corks through which holes 4 millimeters in diameter have been bored. The tubes are placed in a constant-temperature bath at 134.5 ± 0.5°C. so that no more than 6 or 7 millimeters of length project. Each tube is examined by withdrawing about one-half of its length and replacing quickly at 5-minute intervals after 55 minutes have elapsed. The time of the observation which reveals the test paper in any tube to be completely changed to a salmon pink color is recorded as the time of completion of the test. Heating is continued and report is made whether any sample of powder explodes in less than 5 hours. (Standard normal methyl violet papers and standards for salmon pink are secured from the Ordnance Department.)

TABLE 36

APPROXIMATE DIMENSIONS OF A FEW POWDER GRAINS IN MILLIMETERS

Caliber	Length	Diameter	Perforation diameter	Average web
16-inch	58	24	2	5
14-inch	42	18	2	4
12-inch	46	18	2	4
8-inch	33	14	1	2.5
155-millimeter	21	8	0.8	1.5
3-inch	15	7	0.6	1
75-millimeter	10	3	0.2	1
.30-inch	2	1	<0.1	single perforation
.45-inch pistol	Flakes, granular, free from dust.			

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[5] Compare page 238. In other cases this test is also run at 65.5° and 120°C. (see page 249).

Specifications for Smokeless Powder. In addition to comments already made which apply chiefly to straight nitrocellulose powder, specifications for smokeless powders vary with the type. Beyond what has been said of grain size, Table 36 gives the over-all size of a number of powder grains, and Table 37 the web sizes for many more.

The volatiles vary with the web size, as shown in Figure 34. Moisture (see Figure 35) varies both with web size and method of manufacture. For cannon powders, diphenylamine should be 1.0 ± 0.1%, with wider latitude for pistol powders, and the same figure is a maximum for rifle powders. Maximum ash is 0.4%, excluding metal and salts which may be used in small-arms or pistol powders. The heat tests for stability which have been given should be carefully noted.

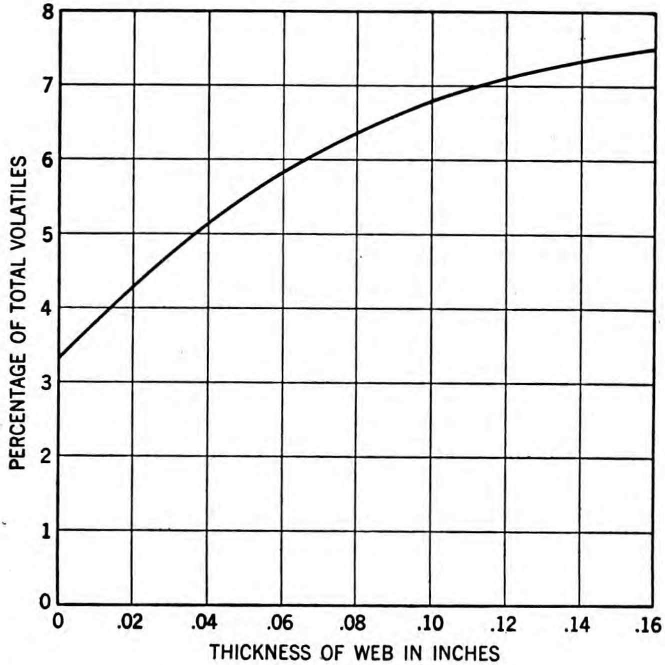


FIGURE 34: **Web Size and Volatiles for Pyrocellulose Powder**

Double-base Powders. *Composition.* The term "double-base" powder has been applied to powders containing nitrocellulose and nitroglycerine as the principal constituents. These powders as used by various military services usually contain from 60% to 80% of

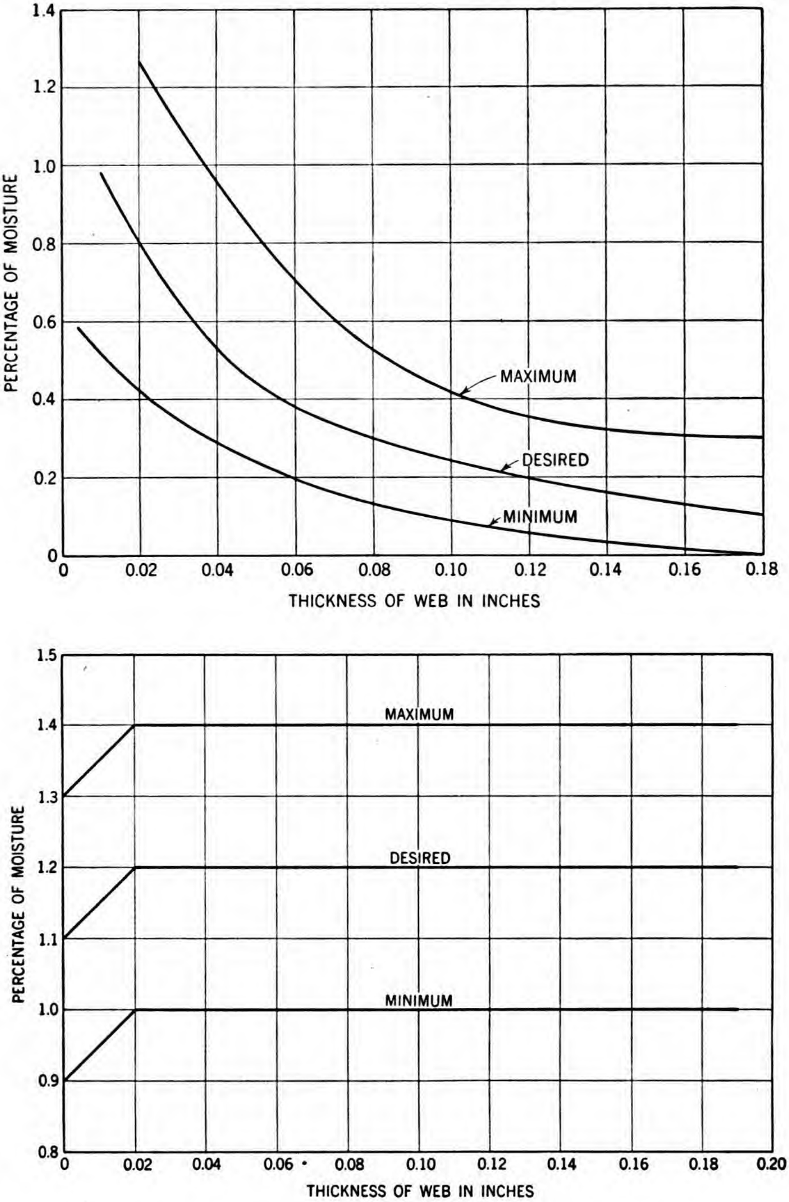


FIGURE 35: **External Moisture and Web Thickness**
(*Upper*) Air-dried, and (*lower*) Water-dried Pyrocellulose Powder.

nitrocellulose and from 40% to 20% nitroglycerine. Certain commercial powders used in sporting ammunition are of similar composition. The nitrocellulose used in double-base powders may be of the pyrocellulose type containing about 12.6% nitrogen or the more highly nitrated type containing above 13.0% nitrogen, commonly referred to as guncotton. Small percentages of inorganic salts such as potassium or barium nitrate are often used in double base powders, these salts serving the purpose of reducing flash or rendering the powder more ignitable. When the percentage of nitroglycerine in the powder composition is small or when the powder is to be extruded, it is customary to use a volatile solvent to colloid the powder. The volatile solvent may be omitted with compositions that contain a high percentage of nitroglycerine and are granulated in thin sheets or disks by rolling, since nitroglycerine is in itself a solvent for nitrocellulose, and the rolling operation colloids the powder to the desired degree.

TABLE 37

WEB RANGE FOR SOME PYRO POWDERS

Weapon	Model	Projectile Wt. Lbs.	Web Size in.
37 mm.	1916	1.234	0.013
37 mm. A.A.	MI.	1.25	0.021 –0.0227
37 mm. Gun	S.A. Tank.	1.25	0.0176
75 mm.	1917	11.72	0.019 –0.027
75 mm.	MI.	14.3	0.031 –0.0322
3″ F.G.	1905	15	0.0238–0.0264
3″ A.A.	M_1M_3	12.7	0.036
105 mm. A.A.G.	M_1	33	0.037
6″ Gun	1908	108	0.064 –0.067
155 mm. Gun	M_1E	95	0.0535–0.0545
155 mm. Howitzer	1918	95	0.0272–0.033
8″ Howitzer	1920 E	200	0.0455–0.0462
12″ Gun	1895	1070	0.1248–0.138
12″ Mortar	1912	700	0.0712–0.078
14″ Gun	M_{11}	1200	0.142 –0.1435
16″ Gun	1919	2340	0.168 –0.173
16″ Howitzer	1920	2100	0.094 –0.095

Characteristics and use. The energy content of nitroglycerine is considerably higher than that for nitrocellulose and, therefore, powders containing nitroglycerine have higher potential than straight nitrocellulose powders, the difference increasing with the percent of nitroglycerine present. The double-base powders are also more readily ignitable and have a higher rate of burning. These characteristics have led to the use of such powders in trench mortars, where especially rapid burning is required. They are also used in certain high-velocity weapons where the high potential of the double-base powders is favorable.

Inspection tests. In the inspection of the double-base powders, the usual chemical-stability and ballistic tests are conducted. Since the chemical and ballistic test requirements vary with the various types of powder but the stability requirements are common to all, the latter requirements only are given.

The heat test at 120°C. is used to determine stability. All powders are required to withstand this test for at least 40 minutes without changing the color of the test paper, and to show no evidence of fumes in 60 minutes. The procedure for this test is as follows: 2.5 grams of the sample are placed in each of two tubes of heavy glass having the following approximate dimensions: length, 290 millimeters; outside diameter, 18 millimeters; inside diameter, 15 millimeters. Each of the tubes is closed with a cork stopper through which has been cut a hole or groove of about 2 millimeters diameter. A piece of standard normal methyl violet paper 70 millimeters long and 20 millimeters wide is placed in each tube so that its lower edge is 25 millimeters above the powder. These tubes are placed in a bath at a temperature of 120.0 ± 0.5°C. so that no more than 6 or 7 millimeters of each tube project outside the bath. The tubes may be examined by withdrawing them about one-half their length outside the bath and replacing them immediately. The tubes are examined every 5 minutes after the first 20 minutes have elapsed. The time in which the methyl violet paper has turned completely to standard salmon pink in either tube is reported. After 60 minutes the tubes are examined against a white background for evidence of fumes.

E. C. Powder. *Composition and use.* This propellant is generally used for loading blank cartridges and hand grenades. It consists of semicolloided nitrocellulose granulated with inorganic nitrates.

Manufacture. The main point observed in manufacture is proper incorporation and mixing of all ingredients. This process is usually conducted by means of a wheel mill in a manner somewhat similar to that used for black powder. Nitrocellulose of approximately 13.15% nitrogen is mixed with about 16% of a mixture of equal parts of potassium nitrate and barium nitrate, together with a small amount of diphenylamine and a pink or yellow coloring matter. The powder mixture is granulated by adding a mixture of water and a suitable solvent to the material in a revolving drum in such a manner that it forms small rounded grains. The nitrocellulose in these grains is only partially colloided, acting as a binding material and hardening the surface of the grains as the solvent is removed.

Granulation. The granulation of E. C. powder is such that the powder will pass a 12-mesh and remain on a 50-mesh screen. A tolerance of 3% is permitted; that is, 3% of the powder may remain on the 12-mesh screen, but the material remaining on the screen must pass a 10-mesh screen, and 3% may pass a 50-mesh screen.

Heat test at 134.5°C. The powder must not turn normal methyl violet paper to a salmon pink color in less than 30 minutes and must not explode in less than 4 hours in this test.

Smokeless Powder as an Explosive. The characteristics of smokeless powder as an explosive are essentially those of pyrocellulose, which has been described, modified by the other materials which may be present. Smokeless powder does not detonate on ignition—that, of course, would be undesirable—but it should be remembered that smokeless powder can be detonated. A fall of 30–45 centimeters of the 2-kilogram weight will detonate it. Its explosion temperature is from a little below to much below that of nitrocellulose (2,710°C.) and may run from 2,400°C. down to 1,940°C. Its explosive strength, measured by tests for *brisant* explosives, may be from 25% under to slightly more than nitrocellulose for nitroglycerine powders; its Q_v = 1,100 to 1,300 Calories per kilogram, and its lead-block expansion is 420 cc.

Discussion Questions and Exercises

1. Tabulate as many properties of the colloidal gel, smokeless powder, as you can, and compare with nitrocellulose.
2. Tabulate the total time required to prepare a batch of smokeless powder.
3. Prepare a flow sheet, from memory, for smokeless powder.
4. Make the usual explosives calculations for the formulae on page 210.

5. Determine the weights of alcohol and ether necessary to make 2,000 pounds of smokeless powder and estimate the recovery.

6. Name some other materials which might have possibilities as stabilizers for smokeless powder to replace diphenylamine. What properties should they have?

8. From the table of approximate sizes and the specifications for grains in Chapter 7, tabulate some exact dimensions for various smokeless powder grains.

9. Be sure that you thoroughly understand the use of the Du Pont nitrometer.

10. Prepare a complete but synoptic outline of the examination of smokeless powder, including grain characteristics, for each type of powder.

11. Elaborate the manufacture of E. C. powder in terms of the previous material.

12. Report on other methods of manufacturing smokeless powder.

CHAPTER 12

T.N.T., Nitro Compounds in General, and Other Explosives, Including Gases

The Cyclic Nitro Compounds. These compounds include the most important military high explosives, but they have also some general application. Trinitrotoluene (1:3:5)—also known as triton, trotyl, trilite, and by a variety of other names—has been an important military explosive since 1904, and is still quantitatively most important. Nitration products of benzene, metaxylene, phenols, anilines, and their substitution products are useful, as well as others. Nitronapthalenes have some applications, among others as stabilizers for nitrocotton, but relatively more is required than of diphenylamine; and in dynamites. Nitrophenanthrenes, nitroanthracenes, and nitro derivatives of more complex hydrocarbons are known, although even from the laboratory standpoint exact identification of complete series of some of the nitro derivatives of the higher hydrocarbons is still uncertain, and they have no large practical use.

Trinitrobenzene (1:3:5) is a more powerful and in many ways more desirable explosive than T.N.T., and would be very useful, were it not for the fact that it is so difficult to prepare by direct nitration. It is practically impossible to manufacture trinitrobenzene economically on a large scale in that way, and it is usually made indirectly from toluene. It is informative to compare the properties of the nitro derivatives of benzene, toluene, and xylene from the standpoint of ease of nitration, sensitivity, and power as explosives. Table 38 presents that comparison and also shows some comparison of these properties with structure.

In our descriptions of these explosive materials, we shall use the following general outline, which is suggested to the student for his study: (*A*) Chemical characteristics of the substance; (*B*) method of preparation, commercial and laboratory; (*C*) explosive reaction, and general explosive characteristics as previously outlined, page 23; (*D*) Government and/or trade requirements; (*E*) standard tests; (*F*) uses.

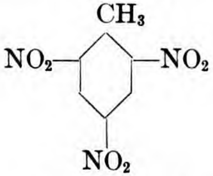
TABLE 38

COMPARISON OF CYCLIC NITRO COMPOUNDS

	Sensitivity cms. for 2 Kg.	Lead Block Expansion, cc. for 15 g.	Velocity of Explosion m. per sec.	Ease of Nitration
Nitrobenzene	> 180			50°C.
Dinitrobenzene 1:3	120	↓	↓	80°C.
Trinitrobenzene 1:3:5	40–50	480	7441	1 day > 100°C.
Nitrotoluene ortho or 2				50°C.
Dinitrotoluene 2:4	↑	↓	↓	80°C.
Trinitrotoluene 2:4:6	57–90	452	7028	3 hrs. at 100°C.
Mononitrometaxylene 2				similar to toluene, but more easily.
Dinitrometaxylene 2:4	↑	↓	↓	
Trinitrometaxylene 2:4:6	170	450	7000	
Trinitronaphthalenes	175	166	about 3,000	80°C.

Calculate and compare Qv, Te, *f*, etc.

Chemical Characteristics of T.N.T. Pure T.N.T.—1:3:5, or 2:4:6 as it is sometimes numbered. The compound meant is always



—is a monoclinic crystalline material, colorless to pale cream, with a melting point of 80.7°C. Commercial grades are darker. United States Army specifications give two grades: I of setting point (see page 260) 80.2°C. minimum, II of setting point 76.0°C. minimum. Grade II can be prepared directly by the nitration process; Grade I must be purified as will be indicated. T.N.T. has a specific gravity of 1.654 and is practically insoluble in water but crystallizes excellently well from alcohol, in which it is very soluble hot and slightly cold, and from other organic solvents. It boils at 240°C. with explosion, but can be distilled under diminished pressure.

The methyl group in T.N.T. is reactive and will undergo many condensation reactions in which two hydrogens are lost by the formation of water with oxygen from another compound, for example nitroso compounds, and aldehydes,

$$\mathrm{(NO_2)_3C_6H_2CH_3 + O{=}N{-}R \rightleftharpoons (NO_2)_3C_6H_2CH{:}N{-}R + H_2O}$$

$$\overset{\mathrm{HOH}}{\rightleftharpoons} \mathrm{(NO_2)_3C_6H_2CHO + RNH_2}$$

These reactions are sometimes highly exothermic and the presence of such materials may cause explosions. T.N.T. and most of the nitrohydrocarbons form very sensitive explosive addition products with alkali, and their presence also is to be avoided.

T.N.T. is definitely toxic, especially for some people, and ventilation and personal cleanliness are necessary in handling to avoid inhalation of vapor and dust and absorption through the skin.

Manufacture of T.N.T.[1] The essential steps in the principal process of manufacture are:

A. Production of mononitrotoluene from toluene.
B. Production of dinitrotoluene from mononitrotoluene.
C. Production of T.N.T. from dinitrotoluene.
D. Washing the trinitrotoluene free of acid.
E. Purification by one of the processes described.
F. Granulation, screening and drying.

Nitration. Several processes are used, for example: (1) The one-stage process, where a large excess of strong mixed acid is used and the temperature gradually raised, with the result that trinitrotoluene is produced in the one process without transfer or separation of spent acid from intermediate products. (2) The two-stage process, where either mono- or dinitrotoluene is produced in the first stage and trinitrotoluene in the second. (3) The three-stage process, where by the use of three different acid mixtures and different conditions of temperature and the like, mono-, di-, and trinitrotoluene are successively produced.

The one-stage and two-stage processes have been superseded by the more practical and more economical three-stage process. A general description of the three-stage process follows:

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[1] U. S. A., TM 9–2900, *Military Explosives.*

First stage. The normal charge used in the manufacture is 1,300 pounds of toluene. The first step in the nitration is accomplished by running into the nitrator approximately 1,200 pounds of mono spent acid. The purpose of adding the spent acid is to provide a very weak charge as a bottom layer so as to prevent stripping the nitrating acid of nitric acid and also to raise the toluene level so that it will come in contact with the cooling coils. If this spent acid is not added, stripping of the nitrating acid is likely to occur, which results in a charred mononitrotoluene. The amount of acid used in the mononitration is based on a ratio of 1 part of toluene to .9 parts of nitric acid. The composition of the mixed acid is 76% sulphuric acid, 23% nitric acid, approximately, water being about 1%. The agitation used during this nitration should be slow enough to prevent mixing of the toluene and the acid; that is, a separating line between these two components should be maintained throughout the nitration. The acid is added through a spider distributor and the temperature maintained at 50°C. during the addition of the first 2,000 pounds, between 50° and 55°C. for the next 4,000 pounds, and at 55°C. for the balance of the charge. The nitration is accomplished by the acid dropping through the toluene. After all the acid has been added, the charge is cooked for 10 minutes, cooled to 45°C., then allowed to settle for 15 minutes, and the acid charge is run off. The acid used in this nitration, where a plant is in continuous operation, is made up by fortifying the spent acid from the dinitration.

Second stage. This stage consists in nitrating the mononitrotoluene to dinitrotoluene. The mononitrotoluene obtained in the first stage is blown from the mononitrating house to the ditrinitrating house and placed in the ditrinitrator. The charge is first cooled to 45°C. The mixed acid used in this nitration is usually a fortified acid made by adding nitric acid to a spent acid from a previous trinitration. The strength of the acid approximates that used in the mononitration, the nitric acid ratio being the same as for the mononitration. The acid is added to the mononitrotoluene and the temperature allowed to increase by 3° steps until it has reached a temperature of 80° to 83°C. It is held at this point for the completion of the nitration. After all acid has been added, the charge is cooked for 30 minutes and cooled to 60°C., settled for 30 minutes, and the spent acid discharged. This spent acid is forwarded to the fortifying house for the addition of nitric acid so that it may be used in the next mononitration.

Third stage. In this stage, the dinitrotoluene is nitrated to trinitrotoluene. It is this stage of manufacture that offers the most difficulty, and extremely strong acids are required to obtain a complete nitration. It is necessary to employ an anhydrous acid. Approximately 3,500 pounds of fuming sulphuric acid is added to the dinitrotoluene oil. This acid is added gradually, the temperature being allowed to rise in 3° steps until a temperature of 80°C. has been reached. As soon as the fuming sulphuric has been added the mixed acid is started. The mixed acid has a composition of 57% nitric and 43% sulphuric, approximately. The nitrating temperature in this stage is 85°C. at the start with a gradual rise in 3° steps until it reaches 104°C. From this point the nitration is continued until a test of the oil shows it has a freezing point of 72°C. or higher. Normally it requires 3 hours of nitration after all the acid is in to obtain this setting point. After this, the charge is cooled to 100°C. and allowed to settle for 30 minutes, after which the spent acid is sent to the fortifiers and the trinitrotoluene oil to the neutralizing house.

Yield. Humphrey[2] states that contrary to usual belief, yield of T.N.T. from the second or dinitration at a given temperature is not a function of the water content of the mixture (except that too strong an acid tends to oxidize the material and in this manner lowers the percentage of yield), but is rather dependent upon the proper low temperature during nitration.

The mononitration yields a product containing a mixture of about 4% of the meta nitrotoluene in addition to the ortho and para isomers. The subsequent nitration changes the meta mononitrotoluene chiefly into the beta and gamma trinitrotoluenes, which differ from the alpha form in chemical properties and are regarded as impurities. Small amounts of other isomers of trinitrotoluene have also been identified in the product of the complete nitration of toluene. Depending upon the completeness with which the last nitration is performed, there may be either a large amount of dinitrotoluene present if improperly carried out, or a relatively small amount if the nitration is correctly done.

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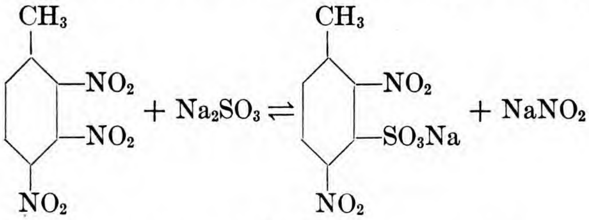
[2] Humphrey, *J. I. E. C.* 8, 998 (1916).

In addition to these impurities, there may also be such bodies as tetranitromethane, which possesses the undesirable property of lowering the solidification point of the pure alpha T.N.T. If the nitration has been properly carried to completion, not more than 4% beta and gamma T.N.T. should be present. This condition is not usually attained under manufacturing conditions and it is therefore necessary to recrystallize the T.N.T. or to purify it by other means in order that the impurities may be eliminated, and a product obtained having the required solidification point for grade I T.N.T. (80.2°C.).

Purification. *Process and equipment.* The crude trinitrotoluene, which, due to the temperature of nitration, is in the form of an oil, is run from the nitrator into neutralizing tubs which have the shape of a cone at the bottom. At the apex of the cone a gateway valve for regular discharge from the tub is provided. Both steam coils for heating and air coils for agitation are provided. Wash water is drawn off by means of suction through a suitable pipe which reaches the tub near the top and extends along the side wall to about 2 feet from the bottom. A small quantity of sodium sulphite can be used to assist in the purification at this point, although it is not necessary to do so. Washing is carried on until no acidity is shown by tests using litmus paper. The neutral T.N.T., in the form of oil, is now pelleted by running it into cold water for transportation to the graining house, or it can be transported in the molten condition to suitable storage tanks through heated pipe lines. If pelleted, these pellets are transported to storage tanks as above mentioned, and again melted before running into the crystallizing kettles. The storage tanks are kept at an approximate temperature of 95°C. and are provided with a gateway screw valve from which the molten charge is drawn off into the graining kettles. These kettles are made of cast iron in one piece, and the junction of the bottom and the side walls is rounded so that plows can scrape the T.N.T. loose from the sides. The lower part of the kettle is fitted with a jacket into which steam or cold water may be discharged. As the plows are started, the charge cools down and the crystals begin to form on the sides; these increase until the whole mass becomes plastic. During the operation all moisture is driven off and the T.N.T. produced is in a fine crystalline condition. It is usually better than grade II; that is, it has a melting point above 76°C. If it is desirable to obtain T.N.T. of grade I, it may be recrystallized from sulphuric acid or another suitable solvent, or treated with sodium sulphite.

Crystallization from sulphuric acid. The fine crystals produced in the graining kettles are dissolved in hot sulphuric acid, usually weight for weight, and cooled. The purified crystals thus settling out are washed free from acid and regrained to such degree of fineness as to pass United States Army specifications. The crude material held in sulphuric acid is accumulated until such time as the amount warrants separate purification.

Sulphite treatment. The sodium sulphite treatment may be applied by taking the fine crystals from the graining kettles and placing them in bins or cars which are equipped with a Filtros bottom. These bins or cars are given one hot-water washing, then four washings with the 5% solution of sodium sulphite, then one warm-water washing followed by sufficient cold-water washings to remove the last traces of the red color which is formed in the treatment. The purified crystals thus obtained can be dried, sieved, and packed, or regrained, as may be necessary to meet specifications. This method of purification is based upon two facts. First, in the nitration of toluene some meta-substituted impurity is always produced. Second, the meta-oriented nitro group in a polynitro cyclic compound is more reactive than others, and will undergo double decomposition reactions, in this case with the formation of water soluble sulphonates; for example:



Laboratory Preparation of T.N.T. The commercial process may be conducted on a laboratory scale as follows:

Using 20% fuming sulphuric acid and commercial nitric acid, 95%, specific gravity 1.5, (*a*) prepare 100 cc. of mixed acid containing 76% H_2SO_4, 23% HNO_3, and approximately 1% of water; (*b*) prepare 50 cc. of mixed acid containing 43% H_2SO_4 and 57% HNO_3.

Mononitration. Put in a small beaker on a water bath 10 grams of the 76–23 mixture, which is to represent spent acid, and add 10 grams of toluene. Bring the temperature to 50°C. Through a dropping funnel just above the surface, add 50 grams more of "spent acid," slowly raising the temperature to 55°C. Keep at 55°C. for 10 minutes after all the acid is added. Cool to 45°C., allow to settle for 15 minutes, and then separate the acid in the separating funnel.

Dinitration. In a beaker on a water bath bring the mononitrate to a temperature of 45°C. Through a dropping funnel add 50 grams of the 76–23 acid mixture, meanwhile raising the temperature slowly by 3° steps until a temperature of 83°C. is reached. Keep at 83°C. for 30 minutes after addition of acid, cool to 60°C. and allow to settle for 30 minutes. Separate in a funnel.

Trinitration. To the dinitrotoluene oil in a beaker over a small gas flame, add slowly through a dropping funnel 30 grams of fuming sulphuric acid (20%), raising the temperature by 3° steps to 80°C. Now through the funnel add 30 grams of 57–43 mixed acid, raising the temperature by 3° steps until it reaches 104°C. Hold at this temperature for 3 hours, or until the oil has a freezing point of 72°C. or higher. Allow the contents of the beaker to settle at 100°C. for 30 minutes and separate the oil. All quantities here can be multiplied by any constant factor.

Purification. Wash the oil with boiling water with stirring until the wash water is neutral to litmus. Then add cold water slowly with good stirring so that the T.N.T. separates in pellets. Weigh and compute the yield. Determine the melting point.

Take one-quarter of the yield and dissolve in an equal weight of hot concentrated sulphuric acid. Cool, separate the crystals using a Gooch crucible, and wash free from acid, using cool water. Determine the melting point.

Take one-quarter of the yield and wash once with hot water, four times with 5% sodium sulphite solution, once with warm water, and then with cold water until free from the red color formed by the treatment. Determine the melting point.

The determination of the solidification point of T.N.T. (see page 261), requires a 50-gram sample. Pure T.N.T. in closed bottles offers no hazards on keeping if it is protected from possibility of detonation.

T.N.T. as an Explosive. In small quantities, on ignition, T.N.T.

burns; but sudden heating will cause detonation, likewise the accumulation of heat in burning large quantities. T.N.T. is one of the most stable of all high explosives and its handling is restricted by few conditions. It requires a fall of up to 130 centimeters of the 2-kilogram weight to explode it. On the other hand, it is a powerful high explosive, producing a lead-block expansion of 285 cc. (10 g.); Q_v = 656 Calories per kilogram; T_e = 2,419°C. It is detonated by such usual detonators as blasting caps, requiring at least a No. 6 for full power, and, for full efficiency in the cast form, the use of a high-velocity initiator as tetryl.

TABLE 39

SPECIFICATIONS FOR T.N.T.

Characteristic	Grade I	Grade II
Color	light yellow to buff	same
Setting point, minimum	80.2°C.	76.0°C.
Moisture	0.10%	same
Acidity	0.10%	same
Insoluble matter	0.10%	same
Insoluble matter retained on No. 40 sieve	0.01%	same
Grit	none	same
Granulation	Crystals: Not less than 95% shall pass No. 14 sieve. Flakes: Average thickness $<.025$ inch., none > 0.04 inch.	
Maximum lot	100,000 pounds	

T.N.T. has an oxygen deficiency, and can explode in several ways (page 99), in common with all the compounds of this group. T.N.T. yields dense clouds of soot on explosion, whereas some of the others have at least enough oxygen to yield entirely gaseous products. Mono- and dinitrotoluenes are added to other explosives for reducing temperature of explosion, to make flashless and permissible explosives.

Analysis of T.N.T.[3] Government specifications for T.N.T. are found in Table 39. Prescribed analysis procedures follow.

Sampling. Select at least 1 box from each 5,000 pounds of packed T.N.T., in no case less than 10 boxes, so as to be representative of the lot. Remove from different parts of each selected box enough of the material to give a sample of about 1 pound; mix this sample thoroughly and place an 8-ounce portion in a bottle so labeled that the box from which the sample was taken can be easily identified. The remainder of each primary sample should weigh about 8 ounces. Mix these remainders thoroughly, and quarter the blend successively until a composite sample of about 1 pound is obtained. Place all samples in tightly stoppered bottles and label each so as to show the name of the material, manufacturer, plant, purchase order and number of pounds in the lot. All acceptance tests are made on the composite sample representative of the lot. Hold the primary samples for possible future examination should the composite sample fail to meet the requirements.

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[3] U. S. A. Specifications 50–13–5C.

Setting point. Place approximately 50 grams of the sample in the inner tube from a solidification-point apparatus. (See both Figure 36 and the description under picric acid, page 271. The same apparatus is used for both of these determinations.) Heat the tube and sample in an oven at 95° to 100°C. for two hours, then place in the solidification-point apparatus. Insert thermometers as shown in the sketch so that the bulb of one, a standardized thermometer calibrated in graduations of 0.1°C. for total immersion, is approximately in the center of the molten T.N.T., and the bulb of the other, a correction thermometer graduated in 1°C., is about one centimeter from and adjacent to the middle of the exposed mercury column of the thermometer immersed in the sample. Stir the sample thoroughout the determination, making approximately 120 complete up and down motions of the stirring rod per minute. Closely watch the thermometer immersed in the sample to determine when the temperature of the sample ceases falling and begins to rise due to the heat of crystallization. Note the temperature of the sample every 15 seconds until the maximum is reached and record this temperature as the uncorrected setting point. Record the reading on the correction thermometer as the average temperature of the exposed mercury column. Calculate the correction for emergent stem as follows:

$$\text{Correction } (^\circ\text{C.}) = n(T - t)(0.000159)$$

where n = number of degrees in exposed mercury column, T = uncorrected setting point, and t = average temperature of exposed mercury column. Calculate the setting point of the sample by adding this correction to the uncorrected setting point.

Moisture. Weigh approximately 5 grams of sample in a glass weighing dish or suitable weighing can. Dry the sample for 8 hours in a vacuum desiccator containing sulphuric acid and weigh. Calculate the loss in weight as percentage of moisture.

Acidity. Weigh approximately 10 grams of sample, melt, shake with approximately 100 cc. of neutral boiling water, and allow to cool. Decant the water and retain. Remelt the sample and extract again with 50 cc. of neutral boiling water. Combine the water extracts, cool, and titrate with a solution of sodium or potassium hydroxide, not stronger than $N/10$, using phenolphthalein as indicator. Calculate the acidity as percentage of sulphuric acid in the original sample.

Insoluble matter. Dissolve a weighed portion of approximately 10 grams of the sample in approximately 100 cc. of benzene or ethyl alcohol. Filter the solution through a tared Gooch crucible. Wash the crucible and residue thoroughly with solvent, dry at 100°C., cool and weigh. Calculate the gain in weight as percentage of benzene or alcohol-insoluble matter.

Insoluble matter retained on No. 40 sieve. Transfer a 100-gram portion of the sample to a beaker and dissolve in benzene or ethyl alcohol. Pour the solution through a No. 40 U.S. standard sieve and transfer any insoluble matter from the beaker to the sieve by means of a jet of the solvent. Wash the insoluble matter on the sieve thoroughly by means of a jet of the solvent. When no more insoluble matter passes through the sieve, dry the sieve and residue remaining on it at 100°C. for one hour. Transfer the dry residue to a piece of paper and then to a tared glass weighing dish. Weigh the dish and from the increase in weight calculate the percentage of insoluble matter in the sample retained on the sieve.

Grit. Transfer the residue, obtained as directed in the paragraph above, from the weighing dish to a smooth glass slide. Rub the material on the glass by exerting pressure with a smooth steel spatula blade. Note whether particles of grit are present as indicated by lack of uniformity and the persistence of a scratching noise when pressing and rubbing of the material on the glass is continued.

Granulation. If the material is in a finely crystalline form, place a metal washer or porcelain crucible lid and a weighed portion of 100 grams of the sample on a No. 14 U.S. standard sieve, attach a bottom pan and cover, and shake the assembly for 3 minutes. Weigh any material retained on the sieve and calculate the percentage passing through the sieve.

If the material is in the form of flakes, measure, by means of a micrometer accurate to at least 0.001 inch, the thickness of each of 100 flakes taken at random from the sample. Note the maximum thickness and calculate the average thickness.

Packing. T.N.T. is packed in (1) rectangular wooden boxes of 50 pounds capacity, complying with the requirements of Interstate Commerce Commission Container Specification No. 14, or in (2) solid fiberboard boxes of 50 pounds capacity complying with Specification 50–61–5, or in (3) fiber drums (approximately 130 pounds capacity) complying with Specification 50–61–4. Wooden or solid fiber boxes are lined with bags having sift-proof bottoms and seams, made from paper at least equal in strength and moisture resistance to the so-called sandwich paper made from two sheets of 30-pound No. 1 Kraft laminated with 30 pounds of asphalt. When the T.N.T. is packed in fiberboard boxes, an additional sheet of protecting paper is provided to cover the entire top of the container. Closure of the fiberboard box is accomplished by coating the entire contact surfaces of the closing flaps with suitable vegetable or animal glue. Precautions are taken so that moist glue does not come in contact with the liner or bag.

Uses. T.N.T. may be regarded as the equivalent of 40% dynamite (sometimes 50%), and can be used under water. It is also used for the detonating fuse known as Cordeau Bickford. For military purposes, T.N.T. can be used for all types of bursting charges, including armor piercing, although it is slightly too sensitive for that purpose and has been replaced by ammonium picrate.

T.N.T. is a relatively expensive explosive. It does not compete seriously with dynamite for general commercial use, but in half-pound blocks it is extensively used for military engineering purposes. For shells it has the advantage that because of its low melting point, it can be melted and loaded by pouring.

Even for military purposes, because of cost, the United States government during the First World War authorized the use of amatol, which is a mixture of T.N.T. and ammonium nitrate, and although increasing supplies of toluene make this no longer so important, 50–50 amatol is still used rather than T.N.T. for shells above 3 inches, and 80–20 for the largest sizes. T.N.T. is also used in mixtures with many other explosives, such as P.E.T.N.; and trimethylenetrinitramine (hexogen and cyclonite), both of which are more powerful than T.N.T.

Amatol. Amatol is more insensitive than T.N.T. but 50–50 amatol is about the same strength, while 80–20 is slightly lower in velocity and *brisance.* The amount of smoke is decreased, and 80–20 produces a white smoke.

Manufacture of 50–50 amatol.[4] The ammonium nitrate as received may contain some moisture and must be dried to a moisture content of not more than .25%. It may also be found that caking has occurred in the barrels or drums in which it has been shipped. To break up the lumps it is often necessary to run the material through a crusher and then dry it to the proper moisture content. After drying, the material is screened to remove any foreign material with which it may have become contaminated. It is now ready for addition to molten T.N.T. The speed of adding ammonium nitrate to T.N.T. can be increased greatly if the ammonium nitrate can be added while it is still hot. It must be added at a rate so that no solidification of the molten T.N.T. takes place in the melting kettle. Proportions for use in mixing 50–50 amatol range from 45% to 55% ammonium nitrate. This variation is permitted to take care of the various granulations, fine material requiring more T.N.T. than coarse material. Temperature of the mixture when it is ready for pouring in the shell is 80° to 85°C.[5]

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[4] U. S. A., TM 9–2900, *Military Explosives.* U. S. A. Specifications.

[5] The melting point of an explosive is a physical property which is frequently of importance in several ways. In the case of nitroglycerine, which is exceptional, the problem of freezing at low temperatures, which has been discussed, presents itself. In general, within limits, the velocity of explosion and therefore, the violence of brisant effects, increases with increasing density. In practice this optimum density is obtained in the loading operation. For an explosive with a reasonably low melting point, in general below 100°C., this can be attained by pouring the explosive as a liquid and allowing it to solidify. Attention must be paid to the contraction on solidifying. The pouring method of loading is a simple and desirable operation. T.N.T. and various of its mixtures, picric acid, and other compounds lend themselves to this. Where it is not possible, loading must be by tamping or extrusion, either of which operation is more complicated,

Manufacture of 80–20 amatol. Eighty-twenty amatol is a plastic mass resembling wet brown sugar and cannot be loaded by the casting method. The principal difficulty experienced with 80–20 amatol is to obtain ammonium nitrate which has proper granulation. With very fine material, plasticity of the mass is such that after loading the density falls below the point desired, namely, not less than 1.38. With coarse material, molten T.N.T. is not completely absorbed and a relatively large amount leaks out in the extruding operation; the result is then a charge of low density. It is therefore essential that granulation be such as to give a mixture which will not permit leaking of T.N.T. and which will be sufficiently plastic to consolidate well from the extruder. It has been found that a mixture of coarse and fine material is the most suitable for this operation. Granulation requirements are: through a No. 10 U.S. standard sieve not less than 99%; through a No. 10 on No. 35, 32% to 48%; through a No. 100, 15% to 30%.

Preparation of 80–20 amatol is conducted in a mixing kettle having a capacity of about 500 pounds of amatol. The correct amount of ammonium nitrate is added to the kettle and heated to the point where solidification of T.N.T. will not occur. When the ammonium nitrate has been raised to at least 90°C., molten T.N.T. is added and the charge is thoroughly mixed for 15 minutes. At the end of this time it is transferred to the extruding machine from which it is forced into the shell by means of a screw working inside of a steel tube. This machine is counterweighted so that the material is forced into the shell under a definite pressure.

Inspection of raw materials. Ammonium nitrate and T.N.T. used in preparation of amatol must conform to United States Army specifications governing these materials, as impurities in both have harmful effects on the resulting product. Oily impurities in the T.N.T. will cause exudation or leakage, while impurities in ammonium nitrate, such as pyridine, cyanide, and the like, will cause formation of gas or frothing, resulting in probable cavitation in the shell. Methods of analysis governing inspection of these materials are given elsewhere (page 198).

Samples. Samples should be taken from the mixer while the stirrers are rotated, as the T.N.T. and ammonium nitrate have a tendency to segregate. It is desirable to take the sample in an aluminum or thin sheet-iron vessel, a circular piece of stout cardboard being placed in the bottom. To obtain concordant results with duplicate analyses, experience will show that extreme care must be taken with the samples.

Tests for moisture. The dish and dome method is used. An aluminum dish and dome (cover) is heated for 15 minutes, cooled in the desiccator and weighed. Approximately 5 grams of the sample is added to the dish, which is placed on the top of a water oven for 3 hours. After cooling in a desiccator for 20 minutes, the weight is taken. Loss in weight equals moisture present in original sample. A small quantity of T.N.T. sublimes but condenses on the inside of the cover, which should be cleaned thoroughly before using in another test.

T.N.T. extraction with benzene. A dry filter paper so folded as to leave a small cavity in the center is weighed in a tared weighing bottle. About 2 grams of powdered amatol is placed in the filter paper without removing it from the bottle, and the bottle is reweighed. The paper and amatol are transferred to a small funnel and washed with approximately 75 cc. of hot benzene, adding enough at a time to cover the powder. After about half the benzene has been added the remainder can be poured in rapidly, taking care to wash thoroughly the sides of the filter paper. The filter paper and residue are transferred from the funnel to the top of a steam oven in order to remove the greater portion of the benzene and dried in a tared weighing bottle for 1 hour. Loss in weight equals T.N.T. plus moisture.

Ammonium nitrate extraction with water. A known weight, approximately 2 grams, is extracted with 50 cc. of hot water at a temperature not less than 85°C. After cooling, the solution is filtered and the process repeated three times with successive quantities of hot water, 50 cc., 30 cc., and 20 cc. The combined filtrates are evaporated just to dryness in a tared dish, and left in a vacuum desiccator overnight. The residue is rinsed two or three times with anhydrous ether, dried on top of the oven to remove ether vapors, cooled, and weighed. The residue equals ammonium nitrate presnt in the sample.

Composition of amatol. Ammonium nitrate was first added to T.N.T. because the latter is a relatively expensive explosive. It had explosive properties and the mixture was cheaper on a weight basis.

T.N.T. has an oxygen deficiency where ammonium nitrate has an excess. It cannot reasonably be assumed that their reaction in a mixture is the same as individually.

T.N.T. has, because of its oxygen deficiency, some uncertainty in its action, but we may assume for it alone the explosion equation

$$C_7H_5(NO_2)_3 \rightleftharpoons 6\ CO + C + 2\tfrac{1}{2}\ H_2 + \tfrac{3}{2}\ N_2,$$

and for ammonium nitrate alone,

$$NH_4NO_3 \rightleftharpoons 2\ H_2O + N_2 + \tfrac{1}{2}\ O_2.$$

It may be supposed that in a mixture the oxygen excess will complete the oxidation of the T.N.T., and there are three possible and significant steps: (1) the oxidation of free carbon to carbon monoxide, (2) the oxidation of the hydrogen to water, and (3) the oxidation of the carbon monoxide to carbon dioxide. In 50–50 amatol there is more than enough ammonium nitrate for (1), and 80–20 corresponds approximately to (3).

TABLE 40

CHARACTERISTICS OF NH_4NO_3 — T.N.T. MIXTURES

Mixture		Property per kilogram		
T.N.T.	NH_4NO_3	n_1	Q_v	T_e, °C.
100	0	40.0	656	2,200
74	26	45.6	674 (1)	2,013
50	50	43.0	815	2,200
45	55	42.4	845 (2)	2,270
20	80	40.0	1,048 (3)	2,300
0	100	43.8	384	1,100

For these reactions the stoichiometrical relations are:

$$C_7H_5(NO_2)_3 + NH_4NO_3 \rightleftharpoons 7\ CO + 2\tfrac{1}{2}\ H_2 + 2\ H_2O + 2\tfrac{1}{2}\ N_2 \quad (1)$$

$$C_7H_5(NO_2)_3 + 3\tfrac{1}{2}\ NH_4NO_3 \rightleftharpoons 7\ CO + 9\tfrac{1}{2}\ H_2O + 5\ N_2 \quad (2)$$

$$C_7H_5(NO_2)_3 + 10\tfrac{1}{2}\ NH_4NO_3 \rightleftharpoons 7\ CO_2 + 23\tfrac{1}{2}\ H_2O + 12\ N_2 \quad (3)$$

By means of the equations and the usual calculations the results in Table 40 may be obtained.

From the standpoint of Q_v and maximum work, the 80–20 mixture would appear to be the best. Because of the lower velocity of explosion of ammonium nitrate there is a loss in *brisant* effect with increasing content, which is slight for 50–50 amatol, but greater for 80–20 amatol despite the high value for Q_v.

Picric Acid. Picric acid, 1:3:5 trinitrophenol, crystallizes in yellow leaflets, specific gravity 1.73, melting point 121.8°C., and explodes on heating. It is slightly soluble in cold water, more so in hot and soluble in alcohol. It is not hygroscopic. It is a direct yellow dye for silk, and stains the parts of the body with which it comes in contact. Externally it is not a poison and is a very good treatment for burns, but inhalation of the dust should be avoided.

Picric acid is acidic and forms salts readily. Many of the salts, known as picrates, are more sensitive explosives than picric acid, especially copper and lead, so it must in general be kept out of contact with metals. Potassium picrate is moderately insoluble in water. Its manufacture is a variation of the usual nitrating procedure.

Manufacture of Picric Acid.[6] Picric acid is made from benzene by two processes, known as the phenol and chlorbenzene processes.

Phenol process. Phenol is prepared from benzene as a raw material by first treating pure benzene with strong sulphuric acid and heating the mixture in jacketed iron kettles provided with agitation at a temperature of about 90°C. for several hours. The resulting benzene sulphonate is usually treated with lime, which converts it to calcium benzene sulphonate, which in turn is converted to sodium benzene sulphonate by means of sodium carbonate (soda ash). The sodium benzene sulphonate is dried and heated in fusion kettles with caustic soda, which converts it into sodium phenate. The fusion mixture is dissolved in water and treated with either carbon dioxide or sulphuric acid, which causes the phenol to separate out as a distinct layer. This layer is drawn off and distilled in order to separate the pure phenol from water and other impurities. Pure phenol is a white crystalline solid which melts at about 40°C.

For conversion to picric acid the phenol is melted into large jacketed iron kettles and treated with sulphuric acid of about 93% strength; the mixture is heated with stirring at a temperature of about 95°C. from 4 to 6 hours. The resulting phenol sulphonic acid is diluted with water and treated in a large acid-proof brick-lined nitrator with 42°B. nitric acid (about 70%). The reaction generates heat and the mixing is therefore carried on very slowly, the maximum temperature being about 110°C. After cooling the mixture, the crystallized picric acid is separated from the spent acid on a vacuum filter, washed with water, and dried.

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[6] U. S. A., TM 9–2900, *Military Explosives.*

Chlorbenzene process. Although this process has been quite extensively used abroad, its use in the United States until recently has been rather limited. Briefly, the process involves initial treatment of benzene with gaseous chlorine, whereby monochlorbenzene results. This product is purified by distillation and then nitrated with a mixture of nitric acid and sulphuric acids to give dinitrochlorbenzene. The latter, on treatment with lime or soda, loses its chlorine and becomes calcium or sodium dinitrophenolate, which on acidifying is converted to dinitrophenol. The dinitrophenol is readily nitrated to picric acid (trinitrophenol) by means of nitric and sulphuric acids.

Uses of Picric Acid. The fact already noted—that picric acid combines readily with some metals to form picrates which are unduly sensitive to friction, shock, or heat—has been a deterrent to the use of picric acid for military purposes in spite of the fact that it is a stronger explosive than T.N.T. The use of a nonmetallic lining for the shell cavity—for example, certain lacquers, varnishes, or paints,—obviates to a great degree the danger of formation of these salts. Introduction of T.N.T. as a military explosive has resulted in gradual abandonment of picric acid by practically every country except France, where it was largely used during the First World War. In the United States picric acid is used for conversion into "Explosive D" or ammonium picrate, which is used in base-fuzed shells for seacoast cannon and in all armor-piercing shells. Picric acid has also found use as a booster explosive and even as a substitute for part of the mercury fulminate charge in detonators.

Picric acid has been used extensively in the form of mixtures with other nitro compounds. Such mixtures, having a lower melting point than picric acid, can be melted and cast at temperatures below 100°C. The mixtures are more generally practical for use because of the hazard involved in melting picric acid at the relatively high temperature required. Some of the compounds which have been used with picric acid are trinitrotoluene, trinitrocresol, trinitrobenzene, and the di- and mononitro derivatives of phenol, cresol, and naphthalene. Little change in *brisance*, if any, results from the addition of the trinitro compounds, but the addition of the mono- and dinitro compounds causes a reduction in *brisance* in proportion to the amount added.

Inspection of Picric Acid. Chemical requirements[7] prescribed for picric acid by United States Army specifications are as follows:

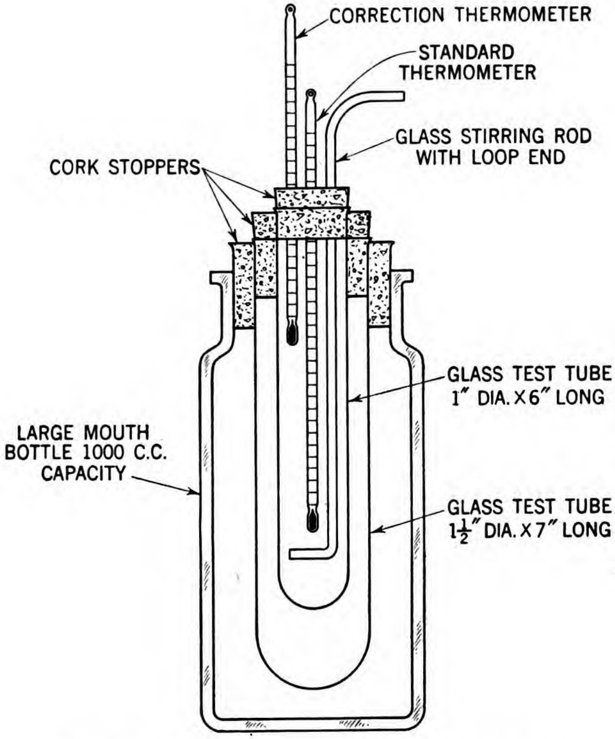
CORRECTION THERMOMETER
STANDARD THERMOMETER
GLASS STIRRING ROD WITH LOOP END
CORK STOPPERS
GLASS TEST TUBE 1" DIA. X 6" LONG
LARGE MOUTH BOTTLE 1000 C.C. CAPACITY
GLASS TEST TUBE 1½" DIA. X 7" LONG

FIGURE 36: **Solidification-Point Apparatus**

(1) It must have a solidification point of not less than 120°C. (2) It must contain: (*a*) Moisture, not more than 0.2% if purchased dry, and not more than 22% if purchased wet; (*b*) sulphuric acid, not more than 0.1%, both free and combined; (*c*) nitric acid, none free; (*d*) ash, not more than 0.2%; (*e*) material insoluble in water, not more than 0.2%; and (*f*) lead, not more than 0.0004%. (3) It must

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[7] U. S. A. Specifications 50–13–2A.

be of a white to yellow color. (4) Not less than 99.5% shall pass a No. 14 U.S. standard sieve.

Methods prescribed for testing picric acid are as follows:

Solidification point. A sample of the picric acid to be used for this test must be dried to constant weight at a temperature not exceeding 50°C. The apparatus used is illustrated in Figure 36. A test tube 1 inch in diameter and 6 inches long is fitted through a cork into a second test tube 1½ inches in diameter and 7 inches long, which in turn is set into a large-mouthed liter bottle. Into the inner tube is fitted a cork stopper through which are three openings. One is in the center, for the standard thermometer, which should be graduated in 0.1°C. One is immediately at the side of the center hole and is for a small thermometer which is passed just through the stopper; the reading of this is taken as the average temperature of the exposed stem of the standard thermometer in making the stem correction. The third hole in the stopper is a small **V**-shaped opening at the side through which passes a wire whose lower end is bent in a loop at right angles to the axis of the tube, for use as a stirrer. The inner test tube is removed and charged with approximately 50 grams of the sample. It is then placed in an oven at a temperature of 130°C. until the picric acid has attained the temperature of the bath throughout. The tube is then assembled in the apparatus for cooling, the standard thermometer immersed in the picric acid with its bulb in the center of the molten mass, and stirring continued vigorously as the temperature falls. The temperatures of both thermometers should be recorded every 15 seconds in order to note the extreme temperature reached on the slight rise of temperature which results during crystallization. This maximum temperature, corrected for emergent mercury column, is taken as the solidification point.

Moisture. A sample of about 5 grams of the picric acid is accurately weighed in a previously tared wide-mouthed weighing bottle at least 1½ inches in diameter, and dried for 5 hours or to constant weight in a drying oven at 70°C. The loss of weight is calculated as percentage of moisture in the original sample.

Sulphuric acid. A known weight of picric acid, approximately 10 grams, is dissolved in 250 cc. of boiling distilled water, acidulated with hydrochloric acid, and the solution is heated. A slight excess of hot solution of barium chloride is then added with constant stirring, the precipitate is allowed to settle, and the mixture is filtered while hot on a tared Gooch crucible. The latter is washed thoroughly with hot water, dried for 3 hours at 100°C., and the weight of $BaSO_4$ calculated as H_2SO_4 in the original sample.

Nitric acid. A water solution of picric acid is tested with a solution of diphenylamine in concentrated sulphuric acid. No coloration should result.

Ash. A known weight of picric acid, approximately 5 grams, is moistened with strong sulphuric acid in a tared crucible and carefully burned until all carbonaceous residue has been eliminated. To compensate for reduction of metallic salts, a few drops of nitric acid and sulphuric acid are added and carefully evaporated; the crucible is again ignited, cooled in a desiccator, and weighed.

Insoluble material. About 10 grams of the sample is dissolved in 150 cc. of boiling water, boiling continued for 10 minutes. The solution is filtered while hot through a tared Gooch crucible, which is washed thoroughly with hot water and dried for 2 hours at 100°C.

Lead. A known weight, approximately 300 grams of the picric acid, is placed in a 2-liter flask and allowed to soak in 100 cc. of a hot saturated solution of barium hydroxide in 65% alcohol. The flask is well shaken, 1,400 cc. of 95% alcohol is added, and the whole is allowed to digest at a temperature below the boiling point of alcohol until all the picric acid has been dissolved with the exception of small particles of insoluble matter. The solution is shaken thoroughly and allowed to stand in the cold until most of the picric acid has crystallized out; then it is filtered. It is not necessary to disturb the crystalline picric acid at the bottom of the flask, as only 500 cc. of the solution is used for completion of the tests and this amount can be decanted. To 500 cc. of this filtered solution, which represents 100 grams of picric acid, four or five drops of nitric acid and 10 cc. of a 1% mercuric chloride solution are added and a slow stream of hydrogen sulphide is passed through this solution for 15 minutes. After allowing it to settle 20 minutes, the solution is filtered and the precipitate is washed with alcohol saturated with hydrogen sulphide; the filter paper is dried and ignited in a porcelain crucible; 9 cc. of nitric acid, specific gravity 1.42, is added and the solution is warmed on a hot plate. Enough warm water is then added to make up the volume to 50 cc. The solution is electrolyzed with a current of 0.4 ampere and

$2\frac{1}{2}$ volts at a temperature of 65°C., using a tared platinum anode. After 1 hour, the electrode is washed by replacing the beaker with another one full of distilled water without interrupting the current. The tared anode is dried and weighed. The weight of lead peroxide, found by difference, multiplied by 0.8661, gives the percentage of lead.

Granulation. A weighed portion of 50 grams of the sample is placed on a No. 14 U.S. standard sieve to which a bottom pan has been attached. Two metal washers are placed on the sieve and shaken for a maximum of 3 minutes, or until no more material passes through the sieve. Any material remaining on the sieve is weighed and the percentage passing through the sieve is calculated.

Picric Acid as an Explosive. Picric acid as an explosive has about the same sensitivity to shock or friction as T.N.T., but is more readily detonated, and is a more powerful explosive. Q_v (probably high) is 810 Calories per kilogram, T_e is 2,430°C., and the Trautzl-block expansion is 305 cc. (10 grams) as recorded. Picric acid may have a detonation velocity of 7,000 meters per second. The explosion reaction may be

$$2\ C_6H_3N_3O_7 \rightleftharpoons 3\ N_2 + 12\ CO + 2\ H_2O + H_2,$$

but it yields a black smoke.

It has been extensively used as a military bursting explosive abroad under various names—lyddite, melinite, shimose—both alone and mixed with such other explosives as T.N.T. and T.N.X., and some mixtures can be loaded by pouring. It is not used much now in the United States. Tridite is 80% picric acid, 20% dinitrophenol, melts at 90°C., and can be loaded by pouring.

Ammonium Picrate. This is the ammonium salt of picric acid. Its use as an explosive is credited to Nobel, by patent, although it had been used before. In the United States it is known as Dunnite or Explosive D. It crystallizes from hot water in yellow-red rhombic needles with a specific gravity of 1.719, decomposing on melting, and exploding at 300° to 423°C. It can react with metals like picric acid, but unless wet the action is slight.

As an explosive, ammonium picrate is marked by great insensitivity, is used for that reason in armor piercing shells, and is the least sensitive of all the military high explosives. The explosion reaction yields some free carbon, but less smoke than picric acid. Q_v is 622, T_e = 2,000°C., lead-block expansion (10 grams) is 275 cc., velocity of detonation is about 7,000 meters per second (but below this probably) as recorded. It is hygroscopic and water reduces its strength and sensitivity. It should be stored in wooden containers or kept in glass in the laboratory, not metal.

Manufacture of Ammonium Picrate.[8] This consists in the main of a simple neutralization of picric acid by means of ammonia, either alone or in combination with ammonium carbonate. This process is not attended with any serious manufacturing difficulties or dangers, provided the possibility of leaking ammonia pipes is excluded.

Details of manufacture are as follows: Approximately 300 pounds of picric acid are mixed with 500 gallons of water at room temperature and then slowly heated by direct steam. As the mixture warms, aqua ammonia is added at the bottom of the tank until neutralization is completed. In some factories it was the practice to add a faint excess, thus insuring complete neutralization of all the picric acid, this condition being evidenced by the formation of a reddish colored crystalline mass of ammonium picrate. United States Army specifications permit a maximum of .025% acidity or alkalinity. When this stage has been reached the resulting material is dropped into tanks for crystallization. These tanks are so equipped that a continual agitation of their contents can be maintained by air with the object of accelerating the crystallizing of the ammonium picrate during the cooling. When the mass has cooled to about 25°C. the crystals are separated from the mother liquor by filtering or draining. From the crystallizing tank the ammonium picrate is taken to the dry house, where it is subjected to a temperature of about 45°C. for 8 hours in drying bins which are so constructed that warm air circulates constantly through the mass. Finally the dried material is screened by means of a rotating screen and sent directly to the packing room. The finished product is then packed in 50-pound boxes lined with waterproof paper and sent to storage.

Reworking ammonium picrate consists in redissolving impure or waste ammonium picrate in water, removing the impurities by filtration, then heating the solution by steam coils until it has been evaporated sufficiently to produce crystallization. From here on the reworking operations are exactly the same as those followed out in the manufacture of the new material.

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[8] U. S. A., TM 9–2900, *Military Explosives.*

Uses of Ammonium Picrate. This explosive is used as the bursting charge for armor piercing shells on account of its insensitiveness to shock, which permits a shell to pass through armor without exploding. Owing to the fact that it cannot be melted without decomposing, it must be loaded into the shell by pressing. The interior of the shell is covered with a suitable nonmetallic paint or varnish. It has no commercial use as an explosive, although it enters into the composition of numerous patented blasting explosives which have not been used to any great extent.

Inspection of Ammonium Picrate. United States Army specifications[9] prescribe the following requirements for ammonium picrate: (1) ammoniacal nitrogen, not less than 5.64%; (2) moisture, not more than 0.2%; (3) solubility, not more than 0.2% insoluble; (4) ash, not more than 0.2%; (5) acidity or alkalinity, not more than 0.025%; (6) color, yellow to red; (7) granulation—(*a*) through No. 14 U.S. standard sieve, 99.5% minimum; (*b*) through No. 100 U.S. standard sieve, 20% maximum.

Tests and determinations covering each of the listed criteria are made on ammonium picrate to determine its suitability for military use.

Ammoniacal nitrogen. A known weight of the ammonium picrate to be analyzed, approximately 1 gram is placed in a 500-cc. Kjeldahl flask (see Figure 37). The flask is equipped with a two-hole rubber stopper which carries an exit tube leading away to a bottle containing $N/10$ sulphuric acid, and an ingress tube reaching to its bottom, through which air that has already been dried and freed from ammonia by passage through concentrated sulphuric acid may be bubbled. Twenty cubic centimeters of water is introduced into the flask, 12 cc. of 5% sodium carbonate solution is added, the flask is set in a boiling water bath, and ammonia-free air is bubbled through until contents of the flask have been evaporated to dryness. The ammonia is absorbed by bubbling the air through 50 cc. of $N/10$ sulphuric acid, a bulb full of very small holes, such as may be made conveniently with a hot platinum wire, being used for the purpose. To deal with the possibility of splashing of the sulphuric acid, the exit tube from the bottle is equipped with a trap. The excess sulphuric acid is titrated with $N/10$ sodium hydroxide, using methyl red or sodium alizarin sulphonate as an indicator, the amount which has been consumed is noted, and the ammoniacal nitrogen in the sample is calculated by the formula:

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[9] U. S. A. Specifications 50–13–3C.

$$\text{percentage of ammoniacal nitrogen} = \frac{1.401\,(AB - CD)}{E},$$

where A = the number of cubic centimeters of sulphuric acid solution in the bottle, B = normality of the sulphuric acid solution, C = the number of cubic centimeters of sodium hydroxide solution used, D = normality of sodium hydroxide solution, and E = weight of sample.

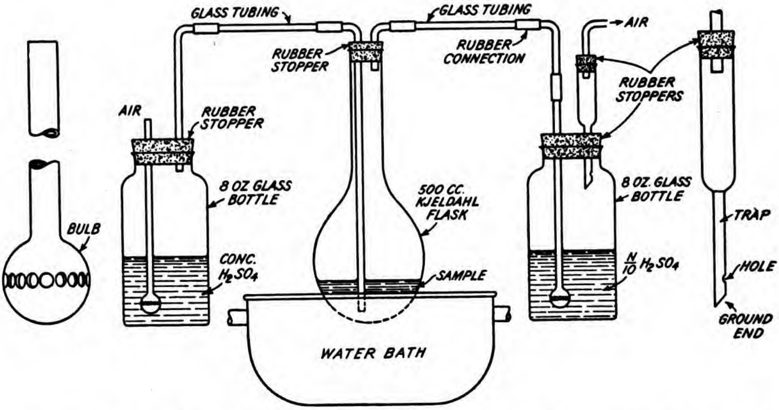


FIGURE 37: **Apparatus for the Determination of Ammoniacal Nitrogen in Ammonium Picrate**

Moisture. A sample of about 5 grams of the ammonium picrate is accurately weighed in a previously tared wide-mouthed weighing bottle at least 1½ inches in diameter and dried for 2 hours or to constant weight in a drying oven at 100°C. The loss of weight is calculated as percentage of moisture in the original sample.

Insoluble material. A known weight, approximately 10 grams, is dissolved in 150 cc. of hot distilled water by boiling for 10 minutes. The solution is filtered through a tared Gooch filter, the insoluble residue washed thoroughly with hot water, and dried for 1 hour at 100°C.

Mineral matter (*ash*). A known weight, approximately 2 grams, is wetted with molten paraffin in a tared crucible and carefully burned until all carbonaceous residue has been eliminated. It is cooled in a desiccator and weighed.

Acidity or alkalinity. A representative sample of 5 grams of the ammonium picrate is ground in a porcelain mortar with 50 cc. of water at room temperature, and the supernatant liquid is poured through a folded filter, the filtrate being caught in a 500-cc. Erlenmeyer flask. This process is repeated until all of the ammonium picrate is brought into solution and the total volume of the filtrate is 250 cc. Three drops of sodium alizarin sulphonate or a 1% alcohol solution of methyl red indicator are added. The solution is shown to be acid if either of the indicators assumes a yellow color. If the solution is acid, it is titrated with approximately 0.1N sodium hydroxide solution and the percentage of picric acid in the sample is calculated according to the formula

$$\text{percentage of picric acid} = \frac{22.905\,AB}{C},$$

in which A = the number of cubic centimeters of sodium hydroxide solution used, B = the normality of the sodium hydroxide solution, and C = the weight of the sample. If the solution is shown to be alkaline by the indicator assuming a purple or red color, it is titrated with approximately 0.1N sulphuric or hydrochloric acid. The percentage of free ammonia in the sample is calculated according to the formula

$$\text{percentage of free ammonia} = \frac{1.7034\,AB}{C},$$

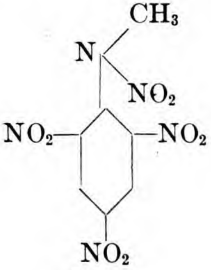
in which A = the number of cubic centimeters of acid solution used, B = the normality of the acid solution, and C = the weight of the sample.

Granulation. A No. 14 U.S. standard sieve is fitted on a No. 100 U.S. standard sieve and a receiving pan attached to the bottom sieve. A weighed portion of 100 grams of the sample and two metal washers are placed on the upper sieve, covered, and shaken 3 minutes. The material retained on the No. 14 sieve and that passing through the No. 100 sieve are weighed and each weight is calculated as a percentage of the whole sample.

Storage of Ammonium Picrate. Storage is governed by the same regulations applicable for the storage of T.N.T., both as to type of magazine and rules for handling, and special regulations governing this particular explosive are not necessary.

Ammonium picrate which has been pressed at a shell-loading plant and removed from a shell is very much more sensitive to shock or blow than new material, and there are cases on record where serious accidents have happened in the loading of shells with ammonium picrate so treated. If it becomes necessary to store this material, special precautions should be observed to protect it against shock or fire, and it should preferably be stored in a building by itself.

Although less sensitive than T.N.T., ammonium picrate can be exploded by severe shock or friction, is highly inflammable, and when heated to a high temperature may detonate. It is therefore necessary that it be treated with proper care as a high explosive.



Tetryl

Tetryl. Tetryl, more properly called trinitrophenylmethyl nitramine, is a very important explosive widely used as a booster, and as a priming charge in addition to fulminate in blasting caps. The prue compound forms yellow crystals, specific gravity 1.6, melting point 130°C., exploding at 187° to 260°C., very slightly soluble in water, but soluble in alcohol and ether. It is toxic and not hygroscopic. Its manufacture properly begins with dimethylaniline, which also nitrates too readily to be treated in the usual way.

As an explosive tetryl is more sensitive to shock than the compounds already described. It frequently explodes with a drop of only 20 centimeters of the 2-kilogram weight but usually runs just below them in sensitivity and above 50 centimeters. The explosion equation may be

$$2\ C_7H_5N_5O_8 \rightleftharpoons 14\ CO + 3\ H_2 + 2\ H_2O + 5\ N_2.$$

T_e is 2,911° to 3,339°C., $Q_v = 908$ Calories per kilogram, and lead-block expansion is 320 cubic centimeters (10 grams). (These are recorded values. On theoretic grounds tetryl might be expected to approximate nitroglycerine. Calculate and compare.) It is more readily detonated than T.N.T. It has a high velocity, 7,229 meters per second, which is the principal reason for its use as a booster, and it explodes by a rifle-bullet impact. It is a definitely toxic material producing anemia and skin eruptions in many workers.

Manufacture of Tetryl.[10] Dimethylaniline is dissolved in a large excess of 96% sulphuric acid. This solution is added to nitric acid or (usually) to a mixture of nitric and sulphuric acid such that nitric acid represents about 30% of the final mix, in a nitrator provided with cooling and agitation. The temperature is kept from 68° to 72°C. (This procedure may be used as the basis for a laboratory method.)

The tetryl is separated from the acid by filtration or by drowning in water and separation. Then the tetryl is given short boiling treatments to reduce the acidity to 0.5% or less. The excess water is removed by filtration and the crude tetryl is purified by crystallization from benzene, acetone, or nitric acid. In recrystallizing, conditions are controlled so that the granulated finished product is free-flowing, to meet the requirements for the manufacture of tetryl pellets in automatic processes.

Inspection of Tetryl.[11] Detailed requirements specify: (1) color, light yellow or buff; (2) melting point, minimum 128.75°C.; (3) granulation, (*a*) through No. 12 U.S. standard sieve, minimum 100%, (*b*) through No. 16 U.S. standard sieve, minimum 95%, (*c*) through No. 100 U.S. standard sieve, minimum 20%; (4) moisture, maximum 0.10%; (5) insoluble matter, maximum 0.10%; (6) acidity, maximum 0.03%; (7) grit, none. Maximum lot is 50,000 pounds.

Sampling is done as follows: Select a minimum of 10 boxes of packed tetryl, or at least 1 box for every 5,000 pounds, so as to be representative of the lot. Sample each selected box by removing from different parts of the box enough of the material to give a primary sample of about 1 pound. Mix this sample thoroughly, and place a 4-ounce portion in a bottle so labeled that the box from which the sample was taken can be easily identified. The remainder of each primary sample should weigh about 12 ounces. Mix these remainders thoroughly and quarter until a composite sample of about 1 pound is obtained. Place the composite sample in a rubber-stoppered bottle and label this so as to show the name of the material, manufacturer, plant, purchase order, and the number of pounds in the lot. All acceptance tests are made on the composite sample representative of the lot. Hold the primary samples for possible future examination should the composite sample fail to meet the requirements.

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[10] For a laboratory method see Tenney Davis, *Chemistry of Powder and Explosives*, p. 177.

[11] U. S. A. Specifications 50–13–4C.

Melting point. Set up a melting-point bath equipped with a mechanical stirrer and a source of heat that can be easily regulated. A beaker of 1 or 2 liters capacity about three-quarters full of clean paraffin oil is recommended. Suspend an accurately standardized thermometer in the bath so that the bulb is not less than 1½ inches from the bottom of the bath; if the mercury column will not be completely immersed at the temperature of the observed melting point, suspend a second thermometer at about ½ inch from, and with its bulb about the height of the middle of the exposed mercury column of the first thermometer.

Grind a small portion (not over 5 grams) of the sample so that it will pass a 100-mesh sieve, and dry it for 2 hours at 100°C. or over sulphuric acid in a desiccator for 48 hours. Use thin-walled capillary tubes of uniform diameter, long enough to extend to the top of the bath. Fill the tube with ground tetryl to a depth of approximately 4 millimeters, compact by tapping, and fasten the tube of the standardized thermometer so that the lower end of the tube is in contact with the bulb of the thermometer. Start the stirrer and heat the bath rapidly to about 120°C., then gradually so that the rise in temperature does not exceed 1° in 3 minutes. Record the temperature observed at the instant the meniscus of melted tetryl first appears across the capillary tube.

If the mercury column is completely immersed at the above temperature, report this temperature as the melting point of the sample. If part of the column is exposed, add the following correction to the observed melting point:

$$n(T - t) \times 0.000159.$$

In this computation, n = the number of degrees in the exposed column; T = the uncorrected melting point; t = the average temperature of exposed column, that is, temperature indicated by a second thermometer; and 0.000159 = coefficient of expansion of mercury in glass.

Granulation. Assemble a nest of U. S. standard sieves Nos. 12, 16, and 100, and fit on a pan. Place 100 grams of the sample on the upper sieve. Cover and shake for 3 minutes. Weigh the material held on and calculate the percentage passing through each sieve.

Moisture. Weigh accurately a sample of about 5 grams in a tared weighing dish of at least $1\frac{1}{2}$ inches diameter, and dry for 2 hours at 100°C., or over sulphuric acid in a desiccator for 48 hours. Calculate the loss in weight as the percentage of moisture.

Insoluble matter. Dissolve a known weight of about 5 grams of the sample in 75 cc. of benzene by heating to about 75°C. and stirring. Cool the solution to room temperature and filter it through a tared Gooch crucible; wash the residue with three 25-cc. portions of benzene, dry to constant weight at 100°C., and calculate the percentage of insoluble matter.

Acidity. Dissolve a weighed portion of approximately 5 grams of the sample in 150 cc. of benzene. Transfer the solution to a separatory funnel and shake with 100 cc. of cold, recently boiled distilled water. Allow the liquids to separate, draw off the water, and wash the benzene solution with another 50 cc. of cold boiled water. Titrate the combined water washes with approximately $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. Calculate the acidity as percentage of sulphuric acid.

Grit. Transfer a 50-gram portion of the sample to a beaker and dissolve in 100 cc. of acetone. Pour the solution through a No. 60 U.S. standard sieve and wash any residue on the sieve with a jet of acetone from a wash bottle. When no more insoluble material passes through the sieve, dry the sieve and the residue remaining on it. Transfer the dry residue to a piece of paper and then to a smooth glass slide. Rub the material on the glass by exerting pressure with a smooth steel spatula blade. Note if particles of grit are present as indicated by lack of uniformity of the material and the persistence of a scratching noise when pressing and rubbing of the material on the glass is continued.

Packing. Tetryl is packed in rectangular boxes or fiber drums of 50 to 100 pounds capacity, lined with strong paraffined paper and so constructed as to comply in all respects with the requirements of the Interstate Commerce Commission regulations.

A *brisance* test was formerly prescribed for tetryl by the sand bomb (see page 377). The nitrometer nitrogen method determines one-fourth of the nitrogen.

Summary of the Nitro Compounds. Mononitrobenzene is readily prepared from benzene, and from it dinitrobenzene. Trinitrobenzene can then be made in poor yields with very large excess of acid by heating at 100°C. for a long time. Trinitrobenzene is more readily prepared by oxidizing T.N.T. in sulphuric acid with chromic oxide. T.N.B. is less sensitive and more powerful than T.N.T. and has a higher velocity of explosion.

Dinitrochlorbenzene and even trinitrochlorbenzene can be prepared by direct nitration, and have some interest. They are powerful explosives which yield phosgene on explosion.

Commercial xylenes are a mixture which is separated by a chemical process to yield metaxylene, which may then be somewhat more easily nitrated to yield a trinitrometaxylene, T.N.X., which has some application.

Explosives more highly nitrated than the tri derivatives of benzene, toluene and xylene can be made with difficulty, but although powerful, they are not used.

Explosives result from nitration of naphthalene; diphenyl and triphenyl; phenols such as cresol and resorcincol; aniline, and a variety of related more complex compounds. Many of these have had minor uses in explosive mixtures; cheddite, for instance, contains nitronaphthalenes and a chlorate. Many homologues of tetryl have been made, of which pentryl (trinitrophenyl-nitramine-ethyl-nitrate), more powerful than tetryl, is the most significant. (See Table 41.)

T.N.T. nevertheless remains as the outstanding military explosive of this group, on a weight basis. This is an over-all evaluation of its characteristics since no single one would ordinarily account for that.

Among its advantages may be included cheapness as compared with other nitro derivatives, ease of manufacture, power, ease of loading by pouring due to low melting point, insensitivity, and stability in keeping and in contact with other materials. Among its disadvantages may be listed cost, which does not enable it to compete with the commercial explosives; difficulty of manufacture, also greater than most commercial explosives; sensitivity, greater, and power, less, than some of the other nitro derivatives; and a very large oxygen deficiency.

These considerations indicate some of the reasons for the employment of the other nitro derivatives, as well as fields for further improvement. Tetranitroaniline, T.N.A. (2:3:4:6), is easier to make, and is a more powerful explosive but more sensitive and reactive. The development of processes for the production of toluene by the cracking of petroleum since the First World War has made T.N.T. cheaper under war conditions than it formerly was.

Picric acid is more powerful than T.N.T. but is much more reactive, in contact with metals particularly. Tetryl is considerably more powerful than T.N.T. but is also more sensitive. Its high velocity of detonation makes it suitable as a booster. Ammonium picrate is less powerful than T.N.T. but is also less sensitive. Homologues of tetryl have been tested and are similar to it. Nitro derivatives of naphthalene and the higher condensed cyclic hydrocarbons in general are less powerful explosives than T.N.T. except at impractically high nitrations. Nitro derivatives of the polyphenyls compare favorably, as well as of the polyphenols and phenol esters, but are expensive. This statement includes diphenylamine and benzidine derivatives. These compounds have indicated applications only where an exceptional characteristic warrants a specific use, even though some of them have higher power than T.N.T.

Gaseous Explosives. Before concluding a survey of explosive materials, some mention should be made of gaseous explosives, although they are in no way chemically related to those just discussed. If this text were written from a theoretical standpoint, it would be necessary to devote a considerable part of the volume to them. And practically, in the field of power generation by the internal-combustion engine, they might be considered even more important than those presented, but we have limited ourselves to the specialized commercial and military uses of explosives.

Explosive single gases are known, for example ClN_3, ClO_2, and C_2H_2, which explode into their constituents, but these are of little practical use or importance, except as the cause of accidents on occasion. Any combustible gas may yield an explosive mixture when mixed with oxygen or air, if the resulting reaction results in a volume

TABLE 41

MISCELLANEOUS NITRO COMPOUNDS

Name	Formula	Molecular weight	Melting point, °C.	Notes
Trinitroresorcinol	$C_6H(OH)_2(NO_2)_3$	245	180	weaker than picric acid
Trinitrocresol	$CH_3C_6H(OH)(NO_2)_3$	243	106	weaker than picric acid
Tetranitroaniline	$C_6H(NH_2)(NO_2)_4$	227	210	similar to tetryl
Ethyl tetryl	$C_6H_2(NO_2)_4N \cdot C_2H_5$	301	96	similar to tetryl
Trinitroxylene	$C_6H(CH_3)_2(NO_2)_3$	241	182	much weaker than T.N.T.
Hexanitro-diphenyl	$C_{12}H_4(NO_2)_6$	424	236	powerful
Trinitronaphthalenes	$C_{10}H_5(NO_2)_3$	263	110	much weaker than T.N.T.
Hexanitrodiphenylamine	$(C_6H_2)_2NH(NO_2)_6$	439	245	powerful

increase and particularly if it is exothermic. The mixture does not have to be a true gas, but may be a colloid suspension; coal dust and flour, are the sources of serious industrial explosions, and any organic dust may be. The explosive system thus set up is subject to the same considerations which govern in the cases we have examined, except that the behavior of the homogeneous and simple ones, as hydrogen and chlorine, is capable today of more exact analysis. Such studies have yielded very important information, and have thrown much light on the exact chemical mechanism of many of the reactions.

TABLE 42

EXPLOSION LIMITS IN AIR

Gas	Volume per cent	
	Minimum	Maximum
H_2	9.55	66.5
CO	16.50	75.0
Water gas	12.50	66.5
Methane	6.00	13.0
Acetylene	3.50	52.5
Pentane	2.50	4.8

The ideal explosion mixture for such systems may be calculated from the equation, for example,

$$H_2 + Cl_2 \rightleftharpoons 2\ HCl,$$

where the ideal composition would be 50% + 50% by volume. Ideal composition for air may be roughly computed on the assumption that air is one-fifth oxygen. In practice, in such cases, it is found that any mixture within what is sometimes called the explosion limits will explode under proper conditions, and these limits vary widely, as is shown in Table 42. The limits are to some extent dependent upon conditions. Practically, however, this latitude in the explosion limits means that the handling of volatile inflammable liquids in quantity, especially in filling tanks where large volumes of nearly saturated vapor are driven from the tanks as the liquid fills them, is a hazardous undertaking, which must be surrounded with such proper safeguards as venting. Numerous and recurring explosions in gasoline filling stations, tankers, and the like testify eloquently to this. The extruded vapor can render explosive a relatively tremendous volume of air, and the gas mixtures can yield violent detonations after any ignition, typically from a static spark. Explosion temperatures may be as high as 4,000°C. under favorable conditions, and effects are comparable to those of high explosives. The effects can be calculated by the procedures already given.

Explosive gas reactions may be catalyzed positively or negatively. Water vapor catalyzes positively the reaction

$$2\ CO + O_2 \rightleftharpoons 2\ CO_2.$$

Lead tetraethyl functions as a negative catalyst in the gasoline-air mixture. The effect is striking when set up as a lecture experiment, using a long hard-glass tube to hold the explosive gas mixture, and the phenomenon is the basis for its use in antiknock gasoline. Gas mixtures usually have a characteristic although variable temperature at which they explode, although this temperature is also a function of the time to which the mixture is exposed to the temperature. The miner's safety lamp operates on the principle of preventing this temperature from being reached. A wire gauze rapidly diffuses the heat of the open flame within and a surrounding gas mixture is therefore not ignited. Explosives can be made permissible for gaseous and dusty mines, by adding materials to reduce explosion temperature, and by selecting explosives for size and duration of flame, the latter being a function of velocity. The Diesel engine operates on the principle of igniting a gas mixture by a compression sufficiently rapid to be adiabatic, thus raising the gas to the explosion point.

As in the case of other explosives, the velocity of propagation of the explosive reaction depends on the nature of the initial impulse, flame, detonator, or the like, and may vary from a few meters to 3,000 meters per second. This velocity varies widely also with pressure and temperature, and many gas mixtures are quite anomalous in their behavior.

Discussion Questions and Exercises

1. Make the usual explosives calculations for these substances and check your results against the statements in the text.
2. Set up formulas for all the possible nitration products of toluene and follow the discussion in the text with your equations.
3. Prepare a report on the relationship of explosive properties to the percentage of nitrogen in the compound.

4. Estimate the time required to produce a batch of T.N.T., and the material cost for 1,000 pounds.

5. Many metallic picrates are quite sensitive to shock. What use does this suggest? They have been so used.

6. Calculate the composition of a mixture of ammonium nitrate and ammonium picrate which would have an oxygen balance. Calculate Q_v and the other explosive values for it. What advantages and disadvantages would it have as an explosive?

7. Make the usual outlines of analysis for these materials.

8. A 70,000 gallon tank is filled with gasoline. Assuming the tank gas to be emitted from the top of the tank in quiet air to occupy a hemisphere, calculate the radius over which an explosive mixture might be found. To what height should a vent pipe be run to ensure safety?

9. Do you think you could distinguish by sound the difference between the explosions due to straight gasoline and "ethyl" gasoline in air? The answer is yes. Describe the sounds.

10. Make the usual explosive calculations for gas-oxygen, and gas-air mixtures, especially for gasoline vapor, assuming it to be heptane or octane.

11. Of what practical importance is the melting point of an explosive?

12. How is the density of an explosive related to its power?

13. Prepare a standard report form based on pages 23 and 253 and report on other explosives such as: hexanitrodiphenylamine, hexogen, pentryl, tetrazene, etc.

CHAPTER 13

Chemistry of Initiators; Explosion Flame

Firing an Explosive. Given an explosive in a situation where it is to be used, the practical problem arises of causing it to deliver its energy at the time and under the circumstances, and in the place in which it will perform to its maximum, with the minimum of disturbance or danger to other surroundings which it is not desired to involve. Since all explosives have some degree of sensitivity, and can release their energy on the application of heat or mechanical energy, part of the desired result could be attained by operating directly on the main charge. In the early days of the use of gunpowder this was done, and guns were fired by the application of a free flame through a hole leading to the powder charge.

The method has, nevertheless, obvious limitations. A free match flame, even though we are past the days of steel, flint, and tinder, is not an easy thing to handle in wind, rain, and other hindering circumstances. The explosive may merely deflagrate on ignition, and not explode. To avoid such failure, mechanical energy of percussion may be employed. But in general it requires a fairly heavy blow of a hammer against a metal surface to provide adequate percussion, and that is not easy to arrange by ordinary mechanical devices, which unless very rugged give comparatively weak percussions.

We might select our explosive materials in terms of the ease with which they could be fired by such direct devices. In that case we should be limited to very sensitive explosives, and their handling in large quantities would be very hazardous. And further, in many cases, we should be using our explosive at very low efficiency indeed, as Nobel found. To fire the most useful high explosives at maximum efficiency requires a more powerful shock than any mechanical percussion can be arranged to give. They need the shock furnished by the high-energy explosion wave of another explosive. This method is initiation by detonation.

The present and obviously efficient answer is to select the main charge in terms of as high a degree of insensitivity as may be possible in the interest of safety, and to use with it an auxiliary charge. This auxiliary explosive is known as an initiator. Igniter, primer, and detonator are terms also applied to the practical devices which do the job; the devices are often combinations of chemical materials with intricate mechanical devices.

This use gives us a new class of explosives, initiators, to be considered at this point. It is also clear that the use of an initiator alone does not solve all of the problems already suggested, and further answers will be apparent.

Initiation by Ignition. Ignition, as has been said, is the oldest method. The heating may be done by a free flame of combustion of ordinary burning material, by an electric heating element, by an electric spark, by heat from mechanical friction, by heat from adiabatic compression of a gas, or by a chemical reaction of a mixture to produce a higher temperature than an ordinary combustion; the last method is then the chemical initiator, and has to be ignited by one of the previous devices if it is to function by ignition. The various methods are not equivalent, and the behavior of the explosive substances toward them varies.

Temperature of ignition is one of the sensitivity tests, as has been seen, and the sensitivity of explosives to ignition and shock varies with different explosives and within sometimes quite wide limits for the same one. Both aspects are of importance. In practice, an initiator should be as certain in its action as is possible to achieve. From the standpoint of safety, the statistical behavior of the individual explosive is important. A large number of explosive materials, including some high explosives, merely decompose on slow gentle heating; a somewhat larger number deflagrate and puff off; very few detonate with any violence. Among those which do detonate are ClO_2, NI_3, P and $KClO_3$, $Hg(CNO)_2$, and $Pb(N_3)_2$, some picrates, and all gas mixtures. Similarly, by contact with a free flame of an ordinary kind, most explosives merely burn with deflagration, often not too rapid. This statement is, however, subject to many limitations. When large quantities (more than a few grams) of any high explosive burn, the accumulation of heat may initiate detonation at any moment. Most explosives can be detonated by sudden heating to high temperatures, or by dropping on red-hot metallic plates, conditions not easy to obtain in practice outside the laboratory. Those explosives which detonate by heating are usually too sensitive to handle practically or too insensitive to use, and experience has sifted the useful ones down to $Hg(CNO)_2$ and $Pb(N_3)_2$.

The action of propellent explosives is essentially in itself combustion, and all the initiation desired is furnished by an initiator which ignites them. Detonation of the initiator is objectionable, particularly where, as in the case of smokeless powder which is a high explosive, it might initiate an unwanted detonation. From this standpoint, the important criteria for an igniting initiator for a propellent explosive are: certain ignition under the primary conditions given and the production of a hot, large flame. From the ballistic standpoint it is important that all of the charge be ignited at once, and this requirement makes the flame characteristics important. Although $Hg(CNO)_2$ (mercury fulminate) is readily initiated by heat and has a fairly hot flame, its flame is of too small size and duration to make it useful for ignition, except where the quantity of main charge is small, as in small-arms cartridges. (Moreover, its sensitivity makes it dangerous in quantity.) Practically, we are largely limited to black powder as an igniting initiator for large charges as in cannon, either alone where a free flame is used, or in combination with other things where the primary impulse is supplied in a different way. Where an electric heating unit is used, for example a platinum heating wire, a mixture of $Hg(CNO)_2$, $KClO_3$, and Sb_2S_3 is often employed to ignite the black powder. The same mixture may be used where the primary source of heat is friction. Where an electric spark or electric heating element is used, a wisp of guncotton, readily ignited by sparks, serves to convey the flame to the powder. Match and scratch mixtures (page 52) may be used to ignite fireworks, usually in conjunction with black powder, which is not too easily ignited by the flame of an ordinary match, particularly when compressed.

Explosive gas mixtures are in general readily ignited by heating, but will nevertheless show some delay. Such mixtures will often withstand exposure to temperatures up to 1,000°C. for as long as 10 seconds before igniting, and even at 2,000°C. the period may be an appreciable fraction of a second. Explosive mine gases may therefore be accidentally ignited by the explosion flame of a blasting charge, but consideration of the phenomenon permits improvement in safety practice. By selecting explosives with as high velocity of explosion as the job permits, and with low explosion temperatures and small explosion flames, or by modifying the fundamental characteristics of the explosive by admixture, one obtains permissible explosives. (See Monobels, page 90 and page 200). All useful explosives, however, have explosion flames which will ignite explosive gas mixtures, and no permissible explosive is *absolutely* safe; it is *relatively* safe when used under proper conditions, which means largely proper loading and tamping, so that the explosion gases have done enough work to cool them considerably before coming into contact with the gas mixture.

Initiation by Percussion. All explosives can be initiated by mechanical shock, although, as we have seen, their sensitivity varies widely. The result of percussion on an explosive is usually detonation, with a more or less loud report in all cases. In carrying out the drop-weight test the principal considerations in determining the amount of explosive to be used are that it should be small enough to be safe and yet large enough to give an audible report. Experiment shows that the amount of the energy obtained by mechanical percussion, while large, is usually only a small fraction of what may be obtained by other methods, particularly from high explosives.

Mechanical devices to deliver a percussion are readily designed, and practically useful. In general, however, such devices, unless too heavy and unwieldy for ordinary uses, deliver a relatively mild blow. The danger of a main charge in large quantity which would be sensitive to such mechanical effects is especially apparent. In fact, of those explosives whose mechanical sensitivity lies within the range of such percussions, which usually means under 4 centimeters of drop for the 2-kilogram weight, or about .02 kilogram-meter of energy, most are too sensitive for safe use even as initiators on a practical scale. The range of choice of initiators to be activated by percussion is, however, somewhat wider than the range of those suitable for ignition. The practical problem is often solved by the use of at least two explosives, one of which reacts to the primary impulse and the second of which initiates the main charge appropriately. In considering the operation of practical devices, it is important to distinguish clearly in one's mind between the primary impulse supplied from the outside and the impulse to be delivered to the main charge.

When a percussion initiator is to be used for igniting a main charge, except for very small charges, it is usually employed in conjunction with black powder, which is fired by the initiator. Familiar percussion mixtures contain:

P and $KClO_3$, useful in fireworks, but too sensitive for general application.

$Hg(CNO)_2$, which in percussion mixtures not intended as igniters is usually used as $Hg(CNO)_2$ 80%, $KClO_3$ 20%, or 90–10, compressed to a density of 2.8. Igniters usually contain also Sb_2S_3.

$Pb(N_3)_2$, which is not generally useful because it requires a relatively heavy percussion for positive initiation, but can be made more sensitive by mixing with other materials.

$Pb(CNS)_2$, $KClO_3$, Sb_2S_3 and T.N.T. mixture, which is used in small-arms cartridges.

Explosion Flame. When an explosive is fired by any means whatever, it immediately produces a large volume of gas, and much heat, which raises the gases to a high temperature. Under these conditions the gases become incandescent and present all of the phenomena which we ordinarily associate with flame. We should naturally expect explosion to be accompanied by flame, and within the range of everyone's practical experience, it is.

The investigation of the flame phenomena in the types of explosives with which we are dealing is a very difficult matter. In the case of gas mixtures in internal-combustion engines, much interesting information has been obtained by building experimental engines with transparent observation windows in the cylinders.

For studying explosives, in general, photography is a useful device, but because of the shortness of time, presents some practical difficulties. Stroboscopic photographs show a practically instantaneous incandescent area which corresponds very closely to the shape of the original explosive; these photos tend to confirm the assumption that the explosion itself takes place at constant volume. This incandescent region spreads out into an irregularly shaped area (volume) much like the impression one gets of the muzzle flash of a gun at night.

Explosion flames differ markedly in size, intensity, and duration, but vary with a variety of factors—including the conditions under which pictures are taken. In general, nitroglycerine explosives, explosives containing metals as does ammonal, and chlorate and perchlorate explosives, as well as gunpowder, give large and brilliant (photographically) flames, but the flame characteristics can be greatly modified by admixture.

The size of the flame depends naturally upon the amount of explosive used; the more explosive the larger the flame. The size of the flame is also proportional to the heat of explosion; so, other things being equal, is the explosion temperature. The duration of the flame is shorter as the velocity of explosion increases.

Flame is a factor which especially concerns igniters, safety of explosives in mines, and flash in the use of guns. Fundamentally, a large durable flame is a characteristic of a given explosive, which can be reduced but not increased. For a given explosive the size of the flame can be reduced by mixing the explosive with inert materials, particularly readily volatile ones with large thermal characteristics. These absorb part of the heat of explosion, and thus also reduce the temperature of explosion. Since they contribute nothing they also reduce the power, but if they are volatile their increase in volume may partially compensate for what would otherwise be a complete loss.

Gunpowder is fundamentally suitable as an igniter. But for permissible mining explosives, since above 2,200°C. the ignition of a mixture of methane and air is practically instantaneous, no explosive with an explosion temperature above that figure can be safe. In practice the allowable limit is lower, around 1,500° to 1,900°C. Explosives with a low flame temperature are obtained from NH_4NO_3. Other explosives may be made permissible by the addition of such materials as $Na_2CO_3 \cdot 10\ H_2O$, hydrated magnesium or sodium sulphate, $(NH_4)_2C_2O_4$, and $CaCO_3$ or $MgCO_3$. By mixing one or more of these, dynamite and blasting gelatin may be made safe for mining use. For mining, especially coal mining, the use of high-velocity explosives is not desirable because too much of the coal is powdered to dust. However, it is worth repeating that limitations as to size of charge and proper conditions of use are as important, if not more important, than the nature of the explosive.

For flashless propelling powder, the addition of inert materials would too greatly lower the potential of the charge, and some cooling can be gotten by the addition of hydrocellulose and an oxygen-deficient explosive such as dinitrotoluene, or by slightly modifying the composition of the powders. Examine the formulas for flashless powders on page 210. A similar reduction in temperature is gotten in dynamites and blasting gelatins by incorporating woodmeal and some such oxidizing agent as a nitrate, although the temperature is thus reduced at the risk of prolonging the flame due to the slower action of the oxidizing agent. As in the case of permissibles, flashlessness depends as much upon use in the gun as upon the powder.

Initiation by Detonation. Initiation by detonation, or sympathetic detonation, is the process of firing an explosive by discharging another explosive very near it or in contact with it. If the characteristics of the initiator are suitable the explosive will be fired with a power which far exceeds any other method of initiation. F. Abel described a classic experiment which demonstrates this fact very graphically. Two properly designed iron cylinders, closed at one end, were loaded under the same conditions with black powder. One cylinder was fired by means of a fuse, the other by a detonator. The detonated cylinder was shattered into fragments, while the other remained whole.

Experiment.[1] *Initiation by detonation, or sympathetic detonation.* A small amount of tetrazine is dropped upon a metallic hot plate which is at a temperature of 220°C. It explodes with a mild report. A small amount of lead styphnate is placed on the plate. It does not explode but will decompose if left too long. Now drop a small portion of tetrazine (Guanynitrosoamino guanyltetrazine) upon the plate near the lead styphnate. The latter explodes with a very loud report. One may experiment with the distance over which the initiation is propagated.

The detonator does not have to be in actual contact with the explosive, as the explosion wave of the detonator will be propagated through air, earth, water, glass, metal, or other materials. The extent to which this propagation will occur depends upon a variety of conditions: the distance becomes larger as the size of the charge increases; moist earth will propagate over several feet, dry earth much less. For positive detonation it is better, however, to have practical contact or separation of only a small fraction of an inch, but in firing large charges, a single detonator may be used, even if the charge is loaded in separate containers, as the detonation can under these circumstances be relied upon to propagate itself if the containers are in reasonable contact. However, propagation by influence sometimes exhibits anomalous effects, and it is hence wiser not to store explosives in the explosive laboratory, even at what seems to be safe distances.

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[1] From A. F. Thompson, Jr., *J. Chem. Ed.*, *20*, *152*, *1943*.

Different explosives differ in their sensitivity to detonation. Certain explosives such as nitroglycerine may be detonated by almost anything, although not at full power; T.N.T. is difficult to detonate and cannot always be relied on to detonate with fulminate of mercury; and ammonium nitrate requires a fairly large detonating charge of T.N.T. or other high explosive. As a rule, for a given quantity of explosive, there is a threshold value at which detonation by some quantity of any initiator begins, although with weak explosion, sometimes so weak that the explosive will not maintain propagation within itself. The use of too weak a blasting cap is a frequent cause of "burned out" shots in practice, and safety precautions practically recommend the use of No. 6 blasting caps as a minimum. Above the threshold value, explosion of the main charge is initiated with increasing proportions of its maximum energy of performance, until a weight of initiator is reached where the main charge exhibits a maximum of performance, and no further increase in the weight of initiator will help. Thus, to detonate a small quantity of guncotton requires 6.5 grams of nitrogen iodide, 3.25 grams of nitrogen chloride, or 0.3 grams of fulminate of mercury, while in detonating 10 grams of nitroglycerine in a Trautzl block test using fulminate blasting caps as detonators (containing 80–20 fulminate-chlorate mixture), the following expansions for given weights of materials were obtained, where 590 cc. was taken as the maximum.

No. 1 cap containing 0.3 g. detonator gave 190 cc.
No. 3 cap containing 0.54 g. detonator gave 225 cc.
No. 6 cap containing 1.0 g. detonator gave 460 cc.
No. 8 cap containing 2.0 g. detonator gave 590 cc.

As the total weight of main charge increases to several pounds or more, a further increase in the required amount of detonator takes place if efficiency is to be maintained. For very large charges this increase would require large quantities. In practice, detonators are chosen so that they can themselves be initiated readily by ignition or percussion, and are therefore sensitive materials. In large quantities, such detonators would be very dangerous to handle, and would confer the danger upon the entire device to which they were attached. In practice, the amount of primary detonator is never increased beyond a few grams, and the additional impulse is supplied by having it fire a secondary detonator in the required quantity, known as a booster. For large quantities of main charge the booster may be several pounds, and boosters must have all of the properties of detonators, except sensitivity to ignition and percussion.

The principal property which determines good initiation by detonation is a high velocity of explosion. The total power of the initiator as an explosive is not as important. For practical purposes, the important detonators are fulminate of mercury, lead azide, P.E.T.N., T.N.T., and tetryl. Of these, fulminate of mercury is not a very powerful explosive but can itself be certainly initiated by heat or percussion; lead azide may be initiated by heat and with difficulty by percussion, although more sensitive mixtures can be made; and the remainder must be initiated by the first two.

In laboratory experiments these considerations are further influenced by a variety of other factors, such as temperature, pressure, physical state (as solid or liquid) of the main charge and of the initiator, powder, crystal mass or cast solid, and volume density under compression. The sum total of such considerations determines the final practical form of the explosive and the choice of the initiator, and even then, for practical purposes, we are limited to the materials as available.

It is worthy of emphasis that, while high velocity of explosion is the principal criterion of good detonators, their action, especially at the threshold, is specific. The order of a series of explosives to different initiators will not always be the same. In general, weight for weight, lead azide as a detonator is much better than fulminate of mercury, the difference being often nearly 10 times, as the figures which appear at the top of page 297 show. Yet to detonate trinitroxylene requires 0.25 gram of $Pb(N_3)_2$, and P.E.T.N. requires only 0.001 gram.

Testing of Detonators. Tests of detonating explosives are essentially tests of *brisance*, involving the ability of the explosive to perforate metallic plates of specified thicknesses.

Explosive	Weight of detonator in grams	
	$Hg(CNO)_2$	$Pb(N_3)_2$
Tetryl	0.20	0.02
T.N.T.	0.25	0.09
Picric acid	0.25	0.03

One test may be conducted thus. An empty copper blasting-cap shell is filled by compression[2] with a given weight (1 gram) of the explosive to be tested. An ordinary fuse is then crimped into position, and the whole arranged so that it stands vertically resting upon a lead plate about 2 inches square and 4 millimeters thick, which in turn rests upon a suitable base which is open beneath the cap (see Figure 38).

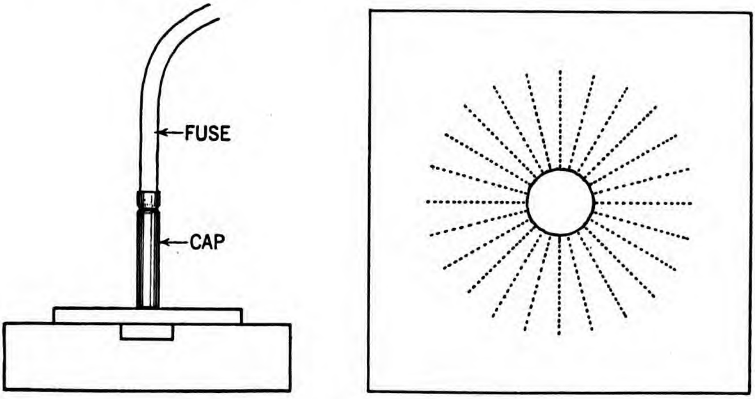

FIGURE 38: **Detonator Test**

When the fuse is fired, the lead plate will be dented or punctured and marked variously. The effect should be compared with a standard detonator.

In this test a good detonator should give a clean hole with divergent ray marks radiating away from it to the edges of the plate. The ray marks are made by the blasting cap shell, which should be pretty well pulverized, and the plate should show no deep markings which indicate the formation of large fragments.

Any of the *brisance* tests may be used, however (see Chapter 16).

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[2] For method of filling and fusing see pages 129, 333, 377.

Choice of a Detonator. Beyond the considerations given, the criteria for the selection of detonators are the same as for the selection of other explosive materials. They must be chemically stable, but of course, being more sensitive than other explosives, all the initiators require very special precautions in handling. They must also be reasonably cheap, but as the amounts used are relatively small, this is not as important as that their raw materials shall be available, and the manufacturing process within practical requirements. The detonator should be as safe, that is insensitive, as the conditions of its use permit. And, as a matter of course where needed, a combination of initiators is made on the basis of the facts of the situation. Thus, if tetryl were required to be fired, it would have to be initiated by fulminate (or lead azide) in practice; in turn it might be desirable to initiate either of these by ignition, and circumstances might require the ignition to be started by the percussion of impact of the device upon a target. This combination of explosives required to meet these conditions is referred to as an *explosion train.* All of the materials in an explosion train must have the characteristics to fit.

Of the various initiators described, we have already considered P.E.T.N., T.N.T., and tetryl, and with the exception of fulminate of mercury and lead azide, the components of the other mixtures are the familiar chemical materials of the general market. We turn then to a consideration of those two.

Fulminate of Mercury. This compound, discovered by Howard (1791), is the mercury salt of fulminic acid, one of four possible isomers of cyanic acid. Liebig in 1823 proved the identity in composition of silver fulminate and silver cyanate, and Berzelius suggested the term isomerism for the phenomenon, in this the first known case. The structure of the isomers later became a matter of interest, especially after four were noted: (*a*) $H\cdot O\cdot C\vdots N$, (*b*) $H\cdot C\vdots N:O$, (*c*) $H\cdot N:C:O$, and (*d*) $H\cdot O\cdot N:C$ or $H\cdot O\cdot N\vdots C$. The problem is complicated by the fact that the same compound or reaction frequently exhibits an equilibrium of two isomers, but it is agreed that formula *d* represents fulminic acid, and mercury fulminate is therefore $Hg(ONC)_2$, although, in practice, while the correct name is used, one does not often see the formula written that way.

Fulminic acid and all of its salts are unstable and decompose with explosive violence, that of mercury being the stablest of the heavy-metal salts, while those of silver and copper are only slightly less so. Mercury fulminate is a white crystalline solid when pure, but ordinarily exhibits a gray to brownish color; it has a specific gravity of 4.4, is practically nonhygroscopic, and almost completely insoluble in water—less than .01 gram per 100 cc. at ordinary temperatures. It may be kept wet under water, when it is much safer to handle, and does not decompose over long periods of time, at ordinary temperatures below 30°C., but in the tropics it may fail to function after 10 months at 50°C.

The chemistry of the manufacturing process is represented by the equations:

$$Hg + 4\ HNO_3 \rightleftharpoons Hg(NO_3)_2 + 2\ NO_2 + 2\ H_2O,$$

and

$$Hg(NO_3)_2 + 2\ C_2H_5OH + HNO_3 \rightleftharpoons Hg(ONC)_2 + 10\ H_2O + \uparrow 8\ NO_2 + \uparrow 2\ CO_2,$$

although the actual mechanism of the reactions is much more complicated.

Manufacture of Fulminate of Mercury. Mercury fulminate is prepared, generally on a relatively small scale, by the action of alcohol on mercury nitrate in nitric acid solution. The raw materials required are metallic mercury, nitric acid, and ethyl alcohol (common grain alcohol of 95% strength). All of these materials must be of high purity in order to produce a satisfactory product.

The process of manufacture is quite simple and may be carried out as follows:

About 1 pound of pure mercury is weighed carefully, added to a weighed charge of from 8 to 10 pounds of strong nitric acid in a suitable bottle or acid pitcher, and allowed to stand until completely dissolved, giving a solution of mercury nitrate in the excess of nitric acid. A large number of such charges are usually prepared and allowed to stand overnight until dissolved.

The acid solution of mercury is then poured into about 8 to 10 pounds of 95% alcohol which has previously been measured into a large thin glass flask or balloon of about 10-gallon capacity supported in a suitable rack under an open shed or in the open air. A violent reaction results, usually within 2 or 3 minutes, the mixture in the balloon appearing to boil violently as a result of the evolution of great quantities of vapors and fumes. These vapors, at first white, become brownish red in color toward the end of the reaction as the heat generated drives off nitric acid. At this point a small amount of dilute alcohol is usually added to prevent excessive heating which would decompose the mercury fulminate produced. The reaction usually lasts about 1 hour. When fuming ceases, the liquid remaining in the balloon is found to contain the crystalline fulminate. In most plants the balloons are placed in troughs of water in order to control the temperature, and the necks of the balloons are connected with a suitable condenser system where the alcohol driven off in the fumes is recovered.

After cooling, the charge in the balloons is dumped onto a cloth screen and washed with cold running water until all free acid is removed and the fine impurities in the form of "fulminate mud" washed away. The washed fulminate is then drained and packed in cloth bags, which are usually stored in crocks of water in vaults, or in underground concrete tanks of water until required for use. For shipment, the bags are packed in barrels of wet sawdust. When required for use, the fulminate is removed from the bags, the water is drained off, and the wet fulminate is spread on cloth to dry in dry houses carefully regulated at a temperature of about 43°C. (110°F.). A pound of mercury produces about 1.25 pounds of dry fulminate. This above-described procedure is readily modified to laboratory scale, but should be done with only a few grams and always kept wet.

Mercury Fulminate as an Explosive. The compound explodes according to the equation:

$$Hg(CNO)_2 \rightleftharpoons Hg + 2\ CO + N_2.$$

It has, therefore, technically an oxygen deficiency, which is improved by the addition of $KClO_3$, and it is usually employed in an 80–20 mixture, to which antimony sulphide may be added when the mixture is used as an igniter. Both addenda also increase the size, intensity, and duration of the explosion flame.

As the first detonating explosive we have carefully considered, the explosive properties of mercury fulminate are of some interest. Experiment seems to indicate that crystal size influences sensitivity. Large crystals appear more sensitive to shock or friction than small ones, and United States Army specifications prescribe size limits.

Finely divided mercury fulminate in the usual process of manufacture is very likely also to contain an excessive amount of impurities, and to be low in sensitivity and also in detonating value.

When used as a detonator, mercury fulminate, whether as crystals or in a mixture, is compressed. The sensitivity decreases markedly with compression. Small amounts of glass increase the sensitivity of the mixture, as gritty particles usually do for explosives. The material is usually pressed to a density of 2.8 which requires at least 250 pounds per square inch, and up to 3,000 pounds is commonly used. If compressed at 25,000 pounds per square inch the fulminate loses its sensitivity almost completely and cannot be certainly fired by percussion or ignition, but may be detonated. However, in compressing fulminate, the pressure must be carefully and slowly applied to avoid explosion.

In terms of the usual sensitivity tests, mercury fulminate detonates by ignition at 210°C., and has a 2-kilogram drop sensitivity of about 5 cm., which makes it the most sensitive material we have thus far considered (except nitroglycerine); in the laboratory, therefore, it must be treated with respect. It should be handled wet as far as is possible, and dried at low temperatures; small amounts of the dry material may nevertheless be handled in the usual laboratory operations with care and with no excessive fear. Large amounts should always be avoided, and residues may be destroyed by warming and then boiling with alkali solution, which completely hydrolyzes the fulminate to harmless compounds.

The explosion temperature of mercury fulminate is given as 3,530°C., which is probably too high, and the Trautzl block expansion for 10 grams is 213 cc. The heat of formation of 1 kilogram of the compound is -221 kilogram calories, from which Q_v may be computed. Its velocity of detonation is 4,000 meters per second, which is only fairly high. While, as has been said, in a general way high velocity of detonation is associated with it, good detonating value is to some extent a specific action. Fulminate is not an especially good detonator. This fact can be seen by comparing the properties of fulminate of mercury with those of lead azide, bearing in mind that except for the practical objection that it is less sensitive, lead azide is on the whole a better detonator in the sense that a smaller quantity will do the same job. The use of fulminate as a detonator would seem to be chiefly due to its sensitivity, not to its other properties.

When the fulminate-chlorate mixture is used in commercial blasting caps, the various sizes contain:

Size No.	Weight of mixture	Size No.	Weight of mixture
1	0.3	6	1.0
2	0.4	7	1.5
3	0.54	8	2.0
4	0.65	9	2.5
5	0.8	10	3.0

grams?

As has been said, caps smaller than No. 6 are not usually sold in the United States; and present blasting caps often have the fulminate charge considerably reduced, to as little as 0.3 gram, and all the remainder replaced by another detonator as tetryl. Such a cap will properly detonate a larger charge than pure fulminate, as well as detonate explosives like T.N.T. which cannot be detonated with certainty by fulminate alone. Other base charges, such as P.E.T.N., are also used instead of tetryl.

Specifications for Fulminate. United States Army requirements[3] for fulminate are as follows: color—white, gray, or gray with a yellowish tint; granulation—retained on a No. 100 U.S. standard sieve, maximum 15%; through No. 200, maximum 75%; in the standard sand bomb test (see page 377) the minimum weight of sand crushed shall be 42 grams, using 0.27 gram to detonate .4 gram T.N.T.; mercury fulminate, 98%; acidity, none; insoluble in sodium thiosulphate solution, maximum 2%; free mercury, maximum 1%; chlorine, maximum 0.05%.

Sampling of Fulminate. Fulminate is packed in barrels containing water, and they must be inspected to be sure they are full and do not leak. Select 10% but not more than 3 of the barrels comprising the lot. By means of a wooden scoop take enough fulminate from different parts of each barrel to give a primary sample of 225 grams. Blend each sample on a smooth surface by mixing with a horn or wooden spatula. Add water in case the sample appears dry. Spread the sample out and divide into squares about $\frac{1}{2}$ inch in size. Take small portions from each square until about 50 grams have been removed. Place this in a bottle and label so as to show from which barrel the sample was taken. The remainder of each sample should weigh about 175 grams. Mix these remainders thoroughly, spread out, mark off into squares, and remove a small portion from each square until approximately 50 grams has been removed. Place this composite sample in a smooth-neck bottle with a tight-fitting stopper, and label so as to show the name of the material, manufacturer, plant, purchase order, and number of pounds in the lot; the last should not exceed 5,000.

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[3] U. S. A. Specifications 50–13–6A.

Laboratory Tests of Fulminate. *Granulation.* A known weight, approximately 10 grams of the dried fulminate obtained by drying to constant weight at a temperature not exceeding 60°C., is added to water and transferred to a 6-inch or some convenient size No. 100 U.S. standard sieve provided with a brass pan, and thoroughly shaken for 10 minutes under water. The residual fulminate is transferred from the No. 100 U.S. standard sieve to a tared filter paper, washed twice with alcohol and once with ether, and dried at 50°C. to constant weight. The fulminate which passes through the 100-mesh sieve is washed on a No. 200 U.S. standard sieve, and well shaken under water for 10 minutes. The fulminate passing through the sieve is transferred to a tared filter paper, washed twice with alcohol, once with ether, and dried in the same manner as the fulminate which remains on the 100-mesh sieve.

Acidity. A known weight, approximately 10 grams of the thoroughly dried material, is placed in a porcelain Gooch crucible provided with a filter-paper disk in place of the customary asbestos mat and washed with two successive 25-cc. portions of boiled distilled water. The filtrate so obtained should show no red tinge upon the addition of three drops of methyl orange solution prepared by dissolving 1 gram of methyl orange in water and making up to 1 liter.

Insoluble matter. A known weight of mercury fulminate, approximately 2 grams, is transferred to a 250-cc. beaker. Then 150 cc. of freshly filtered 20% chemically pure sodium thiosulphate solution at room temperature is added and the solution is stirred for about 1 minute or until the mercury fulminate is apparently in solution. It is then filtered at once through a tared Gooch crucible. Any free mercury remaining in the beaker is completely washed into the crucible with distilled water. The crucible is washed with three or four 10-cc. portions of cold water to free it from sodium thiosulphate and dried at 70°C. to constant weight.

Free mercury. The residue in the Gooch crucible obtained from the insoluble-matter determination is treated with 60 cc. of a sodium thiosulphate-potassium iodide solution containing 6 grams sodium thiosulphate and 3 grams potassium iodide dissolved in water and made up to 50 cc. The solution is decanted through the Gooch crucible containing the insoluble material and the crucible is thoroughly washed with distilled water and dried at 80° to 90°C. for 2 hours and weighed. The residue remaining is taken as the mercury content and the percentage is determined accordingly.

Chlorides. A known weight, approximately 5 grams of the thoroughly dried material, is placed in a porcelain Gooch crucible having in its bottom a filter-paper disk instead of an asbestos mat and washed with two successive 25-cc. portions of distilled water having a temperature between 90° and 100°C. To the filtrate, which is most conveniently caught in a test tube, 3 drops of pure nitric acid having a specific gravity of approximately 1.40, and 10 drops of a 10% solution of silver nitrate are added. No greater turbidity will appear than when a solution containing 0.00042 gram of pure sodium chloride dissolved in 50 cc. of distilled water is treated exactly as the filtrate from the sample of fulminate. This turbidity represents 0.05% of chlorine.

Mercury fulminate. Exactly 0.3 gram of the thoroughly dried material is placed in a wide-mouthed Erlenmeyer flask of approximately 250-cc. capacity, containing approximately 50 cc. distilled water. Next, 30 cc. of a 20% sodium thiosulphate solution, at room temperature, is added quickly and the mixture is shaken for exactly 1 minute and then titrated with standard $0.1N$ HCl solution, using 3 drops of methyl red as indicator.

It is important that the titration begin exactly 1 minute after addition of the thiosulphate. The bulk of the HCl should be added immediately, and the total time of titration should not exceed 1 minute. A blank determination should be run and the necessary correction made. The calculation is as follows:

$$\text{percentage of mercury fulminate} = \frac{0.7116\,(A - B)C}{D},$$

where A = the number of cubic centimeters of HCl used, B = the number of cubic centimeters required for the blank, C = the normality factor for HCl, and D = the weight of sample taken.

Sand test. This test is prescribed for mercury fulminate. It will be described later (see page 377).

Lead Azide. This compound is the lead salt of hydrazoic acid, HN_3, and was first prepared and identified by Curtius in 1891. In 1893 Will and Lenze studied its possibilities as a military explosive. It has been extensively used abroad for many years, and began to be produced in the United States about 1931, but it has not yet come into general use here.

The compound is usually made by a double decomposition reaction with some other substance which is the immediate product of synthesis. Hydrazoates can be made by a variety of reactions.

From sodamide and nitrous oxide:

$$2\,NaNH_2 + N_2O \rightleftharpoons NaN_3 + NH_3 + NaOH$$

From hydrazine nitrate and sodium nitrite:

$$N_2H_4 \cdot HNO_3 + NaNO_2 \rightleftharpoons NaNO_3 + HN_3 + 2\,H_2O$$

These may be regarded as inorganic syntheses of hydrazides. On the other hand, it may be made by organic syntheses:

$$R\text{—}CO\text{—}NH\text{—}NH_2 + HNO_2 \rightleftharpoons R\text{—}CO\text{—}NH\text{—}N(NO)H + H_2O$$

$$R\text{—}CO\text{—}NH\text{—}N(NO)H \rightleftharpoons RCO\text{—}N_3 + H_2O$$

$$RCO\text{—}N_3 + NaOH \rightleftharpoons RCO \cdot OH + NaN_3$$

R may be almost any organic radical, but benzoic and hippuric acids work well in this reaction.

Hydrazoic acid and its sodium salt are soluble in water. All of its salts are unstable, as well as the acid, and decompose explosively. The lead salt, as obtained by precipitation, consists of fine white crystals which are completely insoluble in water. Its hygroscopicity at 30°C. and 90% humidity is about 0.03%. It must be stored wet but keeps much better than fulminate, for at 15 months at 80°C., no loss in sensitivity or power has been noted.

Manufacture of Lead Azide. The first step is the production of sodium azide, usually by the reaction of sodamide and nitrous oxide, gaseous N_2O being passed over sodamide until no more ammonia is evolved. The solid residue is a mixture of NaN_3 and NaOH, which is recrystallized from water.

The production of lead azide from sodium azide is considered one of the hazardous operations of explosive manufacture and is conducted in barricaded equipment. It may be done thus: A 5% solution of lead acetate is placed in a suitable tank equipped with stirring devices, at room temperature. A 2% solution of sodium azide is added slowly. It is customary to add dextrin to the lead acetate solution. This practice produces a yellow-white product which is almost amorphous, exhibiting no crystal faces under a microscope at a magnification of 50×. The lead azide thus produced is technical, 90% to 95% pure, in granular form, and is less dangerous to handle than a purer product.

It is always stored saturated with water, as fulminate is stored. It may be destroyed by the use of a solution of ammonium acetate.

Specifications for Lead Azide. These require: color, white to buff; form, aggregates free from needle-shaped crystals having a maximum dimension greater than 0.1 millimeter; purity, lead content not less than 68.5% nor more than 71.15%; acidity, none; solubility, not more than 1.0% in cold distilled water; sand test (page 377), 0.15 gram detonating 0.4 gram tetryl should crush not less than 45 grams of sand.

Sampling Lead Azide.[4] The method of sampling is similar to that for mercury fulminate, except that 100 grams taken from each barrel is sampled, since the maximum lot is 500 pounds. Of this primary sample, 20 grams is bottled. The remaining portions of the primary sample are blended on a smooth surface by means of a horn spatula. The azide is then spread out and divided into squares about 0.5 inch in size by means of the spatula. Enough azide is removed from all the squares to form a composite sample of 50 grams. This composite sample is thoroughly mixed and transferred to a bottle. This sample represents the lot. The lead azide must be wet during these operations.

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[4] U. S. A. Specifications 50–13–12.

Testing Lead Azide. *Color.* Determine by visual inspection.

Form. Determine by inspection under a microscope, using a magnification of 150. If needle-shaped crystals are observed, measure their maximum dimension by means of a measuring microscope.

Purity. Dry the sample in a steam oven at 95°C. Transfer an accurately weighed portion of approximately 1 gram of the sample to a 400-cc. beaker. Add 50 cc. of a saturated solution of ammonium acetate and dissolve the azide by stirring and warming. Dilute the solution with 200 cc. of distilled water and heat to boiling. Add slowly, with rapid agitation, 10 cc. of a 10% solution of potassium dichromate. Digest on a hot plate or steam bath for 1 hour, with frequent stirring. Catch the precipitate of lead chromate on a tared Gooch crucible, wash with hot distilled water, and dry the crucible and precipitate for 2 hours at 100°C. Cool in a desiccator, and weigh. Calculate the weight of the precipitate in terms of percentage of lead in the sample.

$$\mathrm{PbCrO_4} \times 0.64109 = \mathrm{Pb}$$

Acidity. Transfer an accurately weighed portion of approximately 10 grams of the sample, dried at 95°C., to a tared Gooch crucible. Wash with five 20-cc. portions of cold distilled water which has been boiled prior to the test, allowing each portion of water to remain in contact with the azide for 3 minutes. Add to the filtrate 5 drops of methyl orange solution containing 1 gram of methyl orange per liter of solution. The development of a red tinge indicates the presence of acidity.

Solubility. Dry the crucible and azide from the acidity determination to constant weight, using a vacuum desiccator or a steam oven having a temperature of 95°C. Weigh, and calculate the loss in weight in terms of percentage solubility of the sample.

Sand test. The sand test is prescribed (page 377).

Packing and marking. Lead azide in bulk contains, when packed, not less than 20% of water, and, in this wet condition, is placed in bags of 4-ounce (or heavier) duck, each bag containing approximately 25 pounds (dry weight) of lead azide. In each bag and over the azide is placed a cap of the same cloth and of the diameter of the bag, and the bag is tied securely. Five of these bags are placed in a larger bag of 4-ounce (or heavier) duck, and this large bag is tied securely. The large duck bag contains not more than 150 pounds (dry weight) of lead azide. This bag is placed in the center of a container complying with I.C.C. Container Specification 5 or 5B (metal barrels or drums), 17E (metal drums, single-trip) or 10B (wooden barrels or kegs); the container is lined with a heavy close-fitting bag made of jute or of other suitable bag material of equal strength. The large duck bag is completely surrounded, within the jute bag, by not less than 3 inches of well-packed sawdust saturated with water, and the jute bag is closed by securely sewing to prevent escape of sawdust. The outer container (drum or barrel) is watertight.

When considered necessary, to prevent freezing in shipment and storage, an alternative method of packing is used. The lead azide is wet with not less than 20% its weight of a solution of denatured ethyl alcohol and water containing not less than 33% by weight of ethyl alcohol. The 25-pound duck bags are placed in a strong waterproof bag instead of in a duck bag, and the drum or barrel is filled with sawdust saturated with the same 33% (by weight) solution of ethyl alcohol.

Marking is in accordance with United States Standard Specifications for Marking Shipments, No. 100–2. In addition, each cask or barrel is marked plainly: "Wet lead azide—dangerous."

Lead Azide as an Explosive. Lead azide decomposes according to the equation

$$Pb(N_3)_2 \rightleftharpoons Pb + 3\ N_2.$$

The addition of $KClO_3$, as with fulminate, will improve the quality of the flame by oxidation of the lead. $Pb(N_3)_2$ is one of the less sensitive azides. $Hg(N_3)_2$ is more sensitive than $Hg(ONC)_2$. $Pb(N_3)_2$ detonates by heat at about 350°C., and readily by flame, but its mechanical insensitivity is too great to enable it to be fired by the usual types of firing pins; under a drop-weight test, it may require a fall of 7 centimeters of the 2-kilogram weight. Its molecular heat of formation is -100.6 Calories, from which Q_v may be directly obtained, since the products of reaction are elements. T_e is 4,150°C., and the velocity of explosion is 6000 meters per second.

Lead azide is usually a more efficient detonator than fulminate, weight for weight, and can be used wherever fulminate would be used as a detonator and in priming compositions. Its one drawback is its greater mechanical insensitivity, which can be improved by compounding with other materials.

Other Possible Detonators. Judged by their general properties as an explosive, neither fulminate nor lead azide is a particularly good detonator, and the use of fulminate is probably chiefly due to its ease of initiation. As has been indicated, other high-velocity explosives are coming into use in conjunction with the primary initiator.

In the past much effort has been devoted to the development of new primary detonators and many compounds have been considered, among which should be mentioned acetylides, oxalates, picrates, styphnates diazobenzene nitrate, basic mercury nitromethane, trimercuraldehyde chlorate and perchlorate, as well as other fulminates and azides. But today we still remain largely with the two described.

Initiators, it may be re-emphasized, are the most sensitive of all explosives. They must therefore be handled with great care, and their storage and transportation are hedged about by many regulations, legal, and other.

Discussion Questions and Exercises

1. Why is it useful to emphasize that the behavior of explosive materials is a matter of statistics or probability? What important inference do you draw?

2. Contrast the desirable properties of an ignition or percussion detonator, a booster, a military boosting charge, and a commercial blasting explosive.

3. In what practical ways is the flame aspect of explosives, alone, important?

4. What proportion of Q_v for nitroglycerine would have to be taken care of to reduce its explosion temperature to 1,500°C.?

5. Would you expect $CaCO_3$ or NaCl to be more effective in lowering flame temperature? Why? (Consider all possible absorptions of heat.) What are the various phenomena which can be used for this kind of heat absorption?

6. What does propagation by influence mean?

7. Is it harder to initiate explosion in a granular or a block explosive?

8. Formulate a series of explosion trains for purposes you devise, and tell what you would use for each step.

9. Contrast fulminate and lead azide as detonators. Why is fulminate more used?

10. Summarize the analytic procedures for fulminate and lead azide.

11. Discuss the chemistry of the production of fulminate and lead azide.

CHAPTER 14

Practical Explosive Devices

Introduction. Strictly speaking, the design, construction, methods of manufacture and use of actual explosive devices is perhaps not the field of the chemist, whose point of view is essentially the one presented in this volume. Rather, these belong to the field worker, the engineer, the soldier, and others who are more directly concerned with these tasks. But the chemist must know something about them if he is to be able to appreciate the full significance of the work he is doing and especially if he expects to be able to make useful contributions to the art. It is therefore the purpose of this chapter to present some of the more important general characteristics without entering into a discussion of very specific details which would be more appropriate elsewhere.

General Features. In the most general terms a practical explosive device consists of a *container*, which holds the *main charge*, and some *device for firing* it at the time and under the circumstances when it will most effectively do the job for which it is intended. Devices for firing may be an integral part of the main device or separate from it, but of course must be integrated with it at the point of use. They are important and will be separately treated.

Everyday Uses. For most commercial purposes and some military uses, particularly by engineers, the commonest device for the main charge is simply some conveniently shaped package of uniform standard size. A complete charge is one or more packages, so constructed that when packed together the separation will not prevent a single firing device from exploding all. Thus dynamite and blasting gelatin are commonly sold in the form of cylindrical cartridges wrapped in oiled-paper, of varying diameters and lengths, which have been filled originally either by extrusion of the plastic material from a suitable machine or by tamping. A usual size is $1\frac{1}{4} \times 8$ inches. Nitramon is sold in a cylindrical package of paper with metal ends, whose diameter bears a somewhat larger ratio to its length than the same ratio in the dynamite stick. The ends of the package may have a screw thread, one end male, the other female, so that packages may be put together in one long cylinder. T.N.T. and nitrostarch and other explosives for military engineering use are packed in rectangular packages of cardboard, of $\frac{1}{4}$-, $\frac{1}{2}$-, and 1-pound sizes, with or without metal end pieces. The standard half-pound T.N.T. block is a package $1\frac{29}{32}$ inches square and $3\frac{11}{16}$ inches long. Some others have been described already.

These forms are satisfactory for many uses. To use them, all that is usually necessary is to make up a charge of the proper number of packages tied together, place them where desired, and fire. For underground work, a hole is drilled, and if the required charge is small enough, cylindrical cartridges fit conveniently into the drill hole. If a large charge is needed, however, the process may be more complicated. The nature of the hole may prevent the easy insertion of cartridges and granular explosive may have advantages, in that it can be poured in. Plastic masses have advantages for other uses. These granular or plastic explosives are sold in bulk packages, which may be only paper bags.

Fireworks, to which we have devoted some attention, are practical explosive devices. They usually come as a complete unit, which is set up in an appropriate way, as in a rocket, Roman candle, or bomb, and fired. The device is initiated by lighting with a flame, or rubbing the end of the fuse on a scratch mixture. This initiating device ultimately conveys the ignition to the main charge. Activation is always by ignition, as high explosives are not used in fireworks devices. The main charge is often a complicated series of propellent and incendiary charges, arranged in a container which is designed to produce the desired effects. The containers may present combinations of the principles used in gun, bomb, and flare construction, but since efficiency is not as a rule an important part of the process, the materials of construction are usually paper, cardboard, and wood. Thus a Roman candle on ignition gives off a continuous stream of fire which is usually colored, and at intervals small stars or balls of flame will be emitted from the tube, rise to a considerable height (usually accompanied by a trail of fire), where they may in turn explode with a loud noise into a shower of sparks or into further stars.

Figure 39 shows the design of a Roman candle. From the standpoint of principle, the emitted stars are essentially properly designed shells being fired inefficiently from a cardboard gun which must contain a suitably arranged propellent charge, as well as an intervening incendiary mixture to produce the continuous fire.

Ammunition. Military use of explosives has to do with: (*a*) a military engineering, which presents the same problems and uses much the same form of material as civil engineering; but since military engineers work under military conditions, they cannot usually employ the same explosives, and military explosives have the additional criteria of greater ruggedness as compared to the civilian ones; (*b*) special packages which, in general, it may be said are illustrated by the various kinds of bombs; and (*c*) guns.

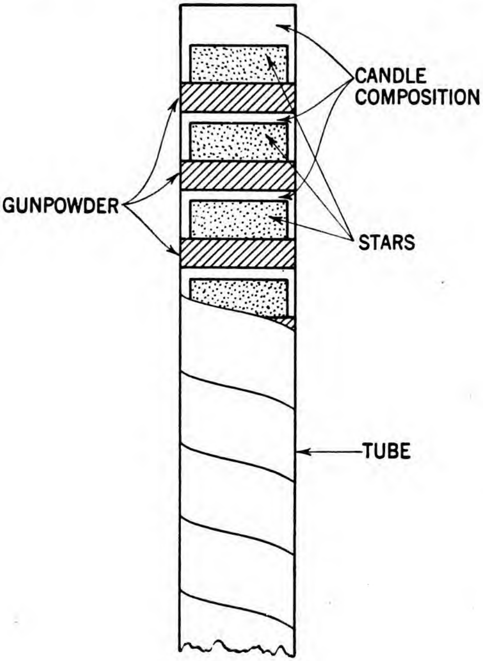


FIGURE 39
Roman Candle

The explosives and impedimenta which go with them, intended for use in connection with guns, are known as *ammunition*. A *round* of ammunition is defined as all of the parts of ammunition necessary for the firing of one shot and consists essentially of three components: a projectile, which may itself contain explosives; a propelling charge to eject the projectile from the gun; and a primer to ignite the propelling charge.

The principal classes of ammunition are fixed ammunition, semifixed ammunition, and separate-loading ammunition.

In *fixed ammunition*, all the components of the round are assembled in a single unit, usually a metal container, in such fashion that it is not intended to be taken apart and it can be loaded into a gun at one operation. The round is often called a cartridge, and the familiar pistol or rifle cartridge is typical. All fixed ammunition looks more or less alike externally although it differs considerably in relative and absolute dimensions, and also in inner content. It is used in all guns up to 5 inches caliber.

As the size of the gun increases, the bulk of the ammunition increases, and it becomes difficult to handle as a single unit. Also there is desirability in modifying the amount of propellent charge for some purposes. *Semifixed ammunition* looks like fixed ammunition except that the projectile is not crimped to the case and may be easily removed, and the powder charge is loaded in separate packages or zones which may be individually removed. It may be used for the smaller field guns, such as the 75-millimeter howitzer. After being put together, it is loaded like fixed ammunition.

In *separate-loading ammunition*, the three component parts of the charge are completely distinct and are put into the gun in separate operations, hence the name. First the projectile is inserted into the breech and rammed hard into the forcing cone at the breech end of the bore; second, the powder charge, in cylindrical cloth bags, is placed in the powder chamber in such a position that when the breech block is closed it is pressed against the propelling charge; third, after the breech block has been closed and locked, the primer is inserted in the firing mechanism of the breech block. The firing mechanism is at the outside end of a longitudinal hole through the breech block. Flame from the primer passes through this hole to reach the propelling charge.

Small-arms ammunition is that intended for guns up to about 20 millimeters caliber. The important types are: ball (which is a misnomer, because the projectile is usually a pointed cylinder), for use against personnel and light targets; tracer, for observations of trajectory and incendiary purposes; and armor-piercing, for attacking armored vehicles, concrete shelters, and other bullet-resisting targets.

Artillery ammunition comprises all the larger sizes. The projectile here is a hollow steel body which may, as will be seen, contain a variety of materials, and in general is known as a *shell*.

Fixed Ammunition. Figure 40 may be taken as an idealized design of all fixed ammunition. It is called a cartridge and consists essentially of:

A cartridge case (*A*), which is usually made of brass.

The ball or projectile (*B*), which is crimped to the case in such a fashion that once it is put together, it cannot be easily taken apart. The ball may be a lead-alloy slug coated with gilding metal, or cupronickel, or it may be very carefully designed with tungsten alloy steel core if it is intended to be armor piercing. In tracer bullets, the rear portion of the ball will contain a smoke and flare mixture with an igniter at the base.

The primer (*C*) which is contained in a cylindrical pellet inserted into the base of the case in assembly. This pellet has at the outside a soft metal plug which is struck in firing by the firing pin, transmits the force to a curved brass piece fitting over another brass piece; between these is the percussion composition. The brass pieces function as a hammer and anvil, and when acted on by the firing pin they apply pressure rapidly. This quick pressure fires the percussion mixture which communicates its flame to the main charge through holes in the anvil. The percussion mixture is usually the lead thiocyanate mixture already described. The plug must not puncture on the blow of the firing pin or the explosion gases would escape to the rear.

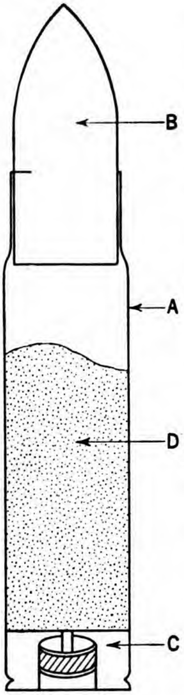


FIGURE 40
Fixed Ammunition

Figure 40 is a center-fire cartridge. Rim-fire cartridges used for cheap ammunition have a projection at the rear of the case which has a layer of the percussion mixture at the bottom extending into the rim. The blow of the firing pin squeezes the composition in the rim as in the anvil, and thus fires it.

The propelling charge (*D*) fills the body of the case, and is held below the projectile by a wad of some kind as for example, paper. The propellent charge is usually smokeless powder, but may be black powder in cheap cartridges, or any propellent explosive.

Figure 41 shows the design of various small-arms cartridges. This

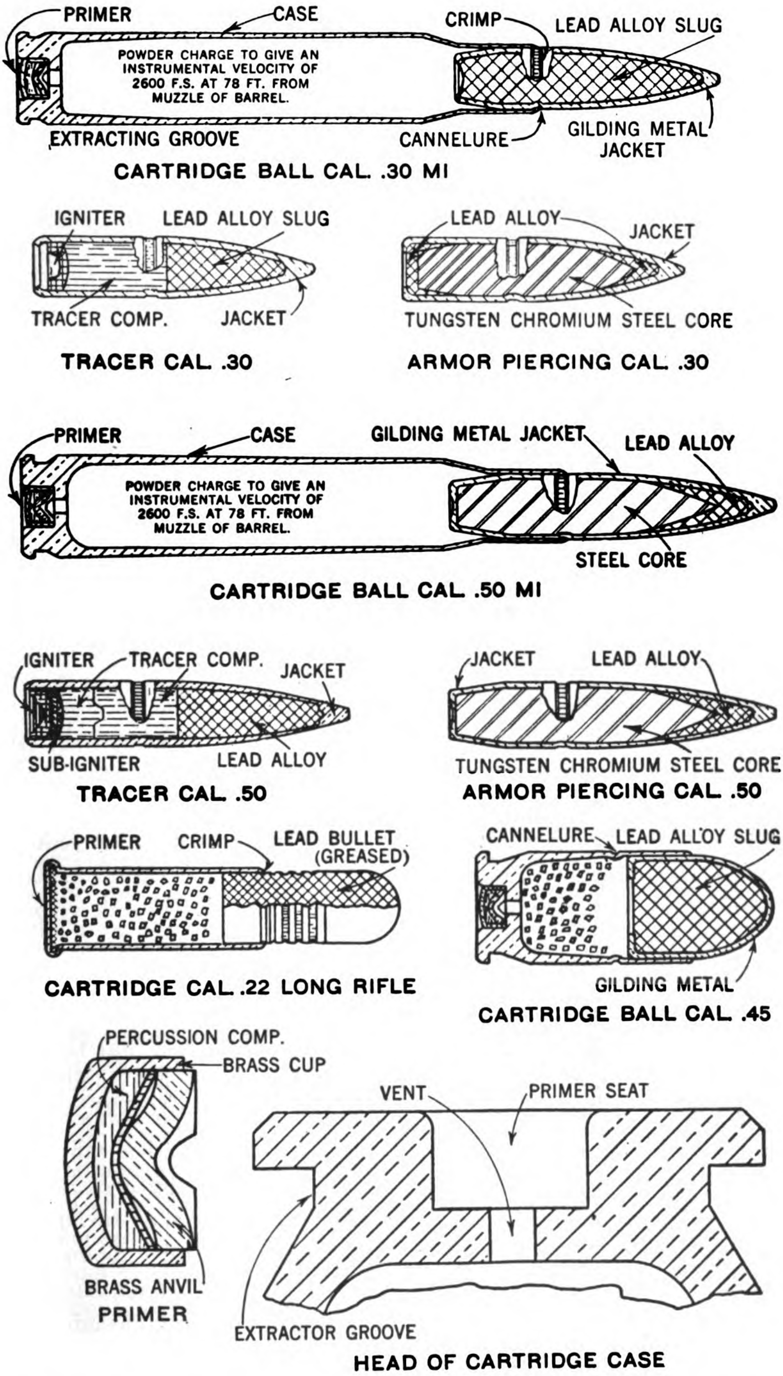


FIGURE 41: **Small-Arms Cartridges and Components (scales differ)** (Reprinted by permission from *Elements of Ordnance*, by Colonel Thomas J. Hayes, published by John Wiley & Sons, Inc.)

design fits all types of fixed ammunition; in cannon sizes, however, the primer is similar in design to those described in the next chapter and contains both percussion mixture and igniter, and the projectile is not of the ball type but rather one of the kinds of shells later described. In fixed ammunition, the cartridge performs many of the functions which are part of the gun's role in a cannon. With fixed ammunition, the essential role of the gun is to provide a seat for the cartridge, and mechanical percussion by the trigger and firing pin mechanism. In the revolver, the bore serves largely as a guide for the projectile, but in other small arms it has much the same role as in the cannon, and helps in the acceleration of the bullet by maintaining the pressure. Actual design in many modern weapons is greatly complicated by the use of part of the expansion force of the explosion gases to aid in providing the percussion force for firing, ejecting the fired cartridge, and replacing it with a new one, and further complicated by the heating and other problems created by the rapid rate of fire thus obtained.

Semifixed Ammunition. This is essentially similar in design to fixed ammunition, except that the projectile is not permanently fixed to the case but is designed to be easily removable. The powder charge is packed in increments something like separate loading ammunition, and one or more parts of the charge can be removed to give a reduced charge which is sometimes desirable. It is used in certain howitzers and mortars, and is a convenient method of adjusting muzzle velocity where such adjustment is necessary.

Guns. Weapons include pistols, revolvers automatic and other, rifles automatic and other, machine guns, mortars, howitzers, and cannon, some of which may be automatic in the sense that they are equipped with various rapid-fire devices. Small-arms are usually said to include everything below 20 millimeters in bore or caliber. The obvious difference between a mortar, a howitzer, and a cannon or gun lies in the ratio, increasing in that order, of length of bore to caliber. For a gun or cannon this ratio is largest; it may be 50 or 60 to 1. Separate-loading ammunition is used for all guns above about 5 inches in caliber, and understanding its use is to some extent dependent upon understanding some features of large-gun design which are essentially the same for all. The detailed features of design and manufacture are important and specialized problems of ordnance and engineering which will not be treated here.

Figure 42 shows an idealized cannon. It consists of the bore (*A*), which is the hollow cylinder through which the projectile travels. This is "rifled," that is, equipped with spiral grooves that give the projectile a spinning motion, and its relative length is an important factor in increasing the velocity of the projectile. The rear of the bore leads to the powder chamber (*B*), and is designed so that in conjunction with the driving band of the projectile which is inserted into the bore, it presents a gastight contact which is preserved as the projectile moves forward so that gases cannot get ahead of the projectile.

The powder chamber receives the powder charge through an opening in the rear, which is closed by the breech block (*C*) fitting tightly when closed. Through the center of the breech block is a generally cylindrical opening (*D*), into which may be fitted tightly the primer which is to fire the charge; this primer will be described in the next chapter. Fitting over the breech block is the actual firing mechanism (not shown), which must contact the primer in whatever way is suitable for firing the primer used. In types using fixed ammunition, the cartridge proper occupies entirely the space indicated as powder chamber while the projectile is in the bore and its primer contacts the firing mechanism.

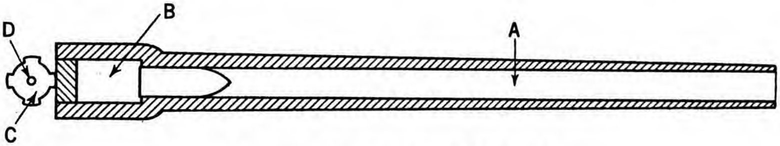


FIGURE 42: **Idealized Cannon**

Separate-loading Ammunition. The Powder Charge. After the projectile is placed properly in the bore, the powder charge is loaded into the powder chamber. The powder charge may be made up in a variety of ways but in no event is it loaded directly in loose grains into the powder chamber.

Powder is usually made up in cartridge bags. Cartridge bags are cylindrical bags of raw silk or cotton, which come in various grades, and some of their characteristics are very important. Inside the bag the powder is usually regularly stacked with grains end to end for the larger guns, instead of at random. The bag itself is closed by sewing or lacing, and filling and closing is done at the arsenals so that in practice the gun crew has the completed bags ready for loading. A charge consists of one or more bags placed end to end to form a cylinder whose diameter nearly but not quite fills the powder chamber. Tie strips may be used to tie the entire charge together, since the charge may consist of as many as five parts.

TABLE 43

OPERATING CHARACTERISTICS OF WEAPONS

Caliber, inches	Artillery			
	Weight of projectile, pounds	Weight of powder, pounds	Velocity, feet per second	Maximum pressure, pounds per square inch
3 (gun)	15	5	2,600	36,000
6 (gun)	105	32	2,800	38,000
8 (gun)	200	71	2,600	38,000
12 (gun)	700	220	2,600	38,000
12 (mortar)	700	63	1,500	37,000
16 (gun)	2,340	882	2,265	38,000
	Small-arms Ammunition			
	Grains	Grains*	Feet per second*	Weapon
.22	27–45	8–15	1,400 up	
.30	220	70	to 3,800	Army rifle
.38	150	40	695	Police pistol
.45	230	50	860	Automatic pistol

* These vary over a wide range with the type of powder, which in commercial cartridges is usually a form of ballistite or E.C. Black powder is employed only for blanks for military and commercial use, and for the cheapest commercial ammunition.

As has been indicated, it is most important that all of the propelling charge be ignited at once. One does not rely on the primer alone to do this. An *igniter pad* is stitched at the end of the charge at the breech, and must fit close to the end of the primer where the primer flame will be certain to ignite the pad. The igniter pad comes separately from the charge, although it may be pinned to it, and is attached properly during loading.

The igniter pad is made of cartridge-igniter cloth (pure silk or substitute) filled with black powder. The cloth must be more closely woven than cartridge-bag cloth to prevent the powder sifting through. The igniter may also be a cylindrical core of black powder within the cartridge bag.

One desirable characteristic of the bag cloth is that it must burn completely without leaving smoldering fragments after the charge is fired. After a firing of the gun, the chamber and bore are filled with the explosion gases which contain considerable CO and other combustible gases. When the breech block is opened, air is admitted, which forms an explosive mixture that might be fired by any smoldering fragments of the bag, or by its own temperature. This phenomenon, known as flareback, has been the cause of serious accidents. Guns may have compressed air mechanisms to sweep out the explosion gases before opening the breech block.

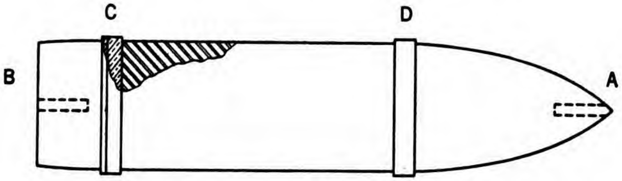


FIGURE 43: **Idealized Shell**

Table 43 gives a summary of size of powder charge, weight of projectile, and other illustrative characteristics of some guns.

Separate-loading Ammunition. Projectiles. The projectile fired by the larger guns is usually itself an explosive device, known as a shell. Shell characteristics and design are a highly diversified problem, but Figure 43 illustrates the general characteristics of an idealized shell. Its principal essentials are a cylindrical metal case, which contains the main charge or charges, and a fuze, which may be fitted into the nose at *A* or at the base *B*; that is, the shell may be point-fuzed or base-fuzed. The point, known as the ogive, has a circular curvature whose radius is along a perpendicular to the horizontal axis of the diagram. Behind the ogive is a projecting surface known as the *bourrelet* (*D*), and toward the rear is another projecting surface

(*C*) known as the driving or rotating band. These are the only two parts of the shell which touch the bore of the gun in operation. The driving band is made of copper or soft metal and in loading fits snugly against the bore. When the charge is fired it first prevents the shell from moving; then, as the pressure rises and the shell moves forward, the rifling of the barrel cuts into the soft metal of the driving band, squeezing it back into grooves designed to receive it and at the same time maintaining a close fit, or as it is said, the rifling "engraves" the band. As the shell moves forward, the *bourrelet* centers the forward end of the shell. To give it better ballistic characteristics, the shell may be tapered behind the driving band, or "boat-tailed." The fuze is a separate device, which is attached immediately before use by screwing it into a threaded fitting prepared for it. It should fit with the exertion of very little force. The fuze is also a separate device in the larger fixed ammunition, which, of course, must be point-fuzed.

Shells and bombs, some of which are described here, may be classified according to their function or behavior and their contents.

Armor-piercing shells are characterized by a very sharp nose (usually covered with a longer false windshield, as a long nose gives better ballistic properties but has poor penetration) and heavy walls, and are boat-tailed. In every way from the standpoint of materials and design, they are very carefully built, to meet the problem of penetrating heavy steel armor as well as possible under all circumstances of flight. They are always base-fuzed. The explosive charge must be insensitive enough to withstand not only the shock of propellent discharge, but also that of impact at high velocity with heavy steel armor plate. T.N.T. has been used, but is a little too sensitive, and armor-piercing shells usually contain a bursting charge of ammonium picrate, with a tetryl booster.

High-explosive shells are intended for use against personnel and other targets which do not demand extreme degrees of penetration. They may be made long nosed and of ordinary steel, with relatively light walls. They may be either point-fuzed or base-fuzed. The main explosive charge, with increasing shell size, may be T.N.T., 50–50 amatol, or 80–20 amatol with a tetryl booster.

Chemical shells are similar in general design to the high-explosive shells. The main charge consists of the chemical, which may be one of the usual "poison" gases (that is a lachrymator, vesicant, or the like), or a smoke-producing compound. Chemical shells are always point-fuzed, and contain in addition to the fuze only enough high explosive to shatter the shell and distribute the solid or liquid main charge in atomized condition in the immediate vicinity. Any of the high explosives may be used.

At the close of the First World War, more than half of all the cannon shells used were chemical shells. Up to this writing in the present war this has not been true. To May, 1942, there were no definite proofs of the use of gas by the Germans at all, and only some instances of use by the Japanese on a small scale. Reports after that begin to multiply and it seems likely that before the termination of the conflict this type of shell will again be important.

Illuminating shells are fuzed to explode during flight. The small bursting charge releases a flare mixture suspended by a parachute, which burns with an intense light lasting several minutes as the parachute drifts slowly downwards, illuminating the area.

Shrapnel shells are used for some of the smaller-caliber cannon, including antiaircraft, but are becoming obsolete. The cylindrical shell is point-fuzed. The main portion of the shell is filled with steel balls imbedded in resin, which is poured over the balls in loading. At the base of the case is a main charge of black powder, to which an igniting flame is carried by a cylindrical tube which runs through the center of the shell from the fuze. A diaphragm is ahead of the steel balls. When the fuze ignites the powder charge, the shell is not fragmented, but the diaphragm and entire nose of the shell are blown forward, followed by the steel balls, which spread out like buckshot in a widening cone. The shell functions something like a shotgun.

All of the described shells come in various sizes and weights and in general are expensive devices, costing several thousand dollars each for larger sizes. Special target-practice or dummy shells may be used, which are made of cheaper materials and loaded with sand to maintain weight. They may or may not be intended for ejection from the gun, and guns may be fitted with subcaliber projectors and use subcaliber projectiles in practice.

Loading of Shells. The manufacture of shells and other explosive devices is a large and important industry. After the shell is made it has to be filled with the main charge. An advantage of explosives like T.N.T., and 50–50 amatol is that they are liquid at reasonably low temperatures and shells may be filled by pouring the liquid into them. This filling may be done by hand by workmen using buckets of the liquid material. There is some contraction on solidifying and the resultant hollows must be filled up; otherwise the shock of "set-back" of the explosive in such spaces may be sufficient to explode the charge as the shell is ejected from the gun. Such an occurrence would, of course, be a serious accident.

Other explosives have to be loaded by tamping, that is, by running the charge into the container and pressing it heavily to the required density in successive operations until the shell is full. Plastic explosives may be loaded by extrusion in machines which operate on the same principle as that by which we eject toothpaste from its container. The loading operation presents more or less hazard depending on the nature of the explosive. When care is observed in manufacture so that the sensitivity of explosives is not greater than it should be, industrial poisoning is a statistically greater risk than explosion, since the military explosives are generally rugged materials; but there are explosions from time to time. The increase in the number of explosions in war times is to be ascribed in general rather to the inexperience of new workers than to sabotage or essential danger.

Grenades. The general principles exhibited by shells are more or less characteristic of all military explosive devices, which differ essentially only in size and design. The grenade is merely a small shell or bomb, consisting of container, main charge, and fuze, but has a relatively limited number of applications. In the familiar Mills or fragmentation hand grenade, a corrugated cast-iron container is designed to fragment on explosion; it is generally egg-shaped, and about large enough to fit into the hand. It weighs about 8 ounces over-all. A lever on the side of the grenade is held in place by a cotter pin, which can be removed, and the lever turned. This turn actuates the firing pin, which explodes a percussion charge that in turn ignites a time train, taking about 8 seconds to fire the main charge. The trick is to throw the grenade in such a manner that it will arrive at its objective at about the time it is to explode, and neither too late which is serious for the user, nor too early, lest it be picked up and thrown back.

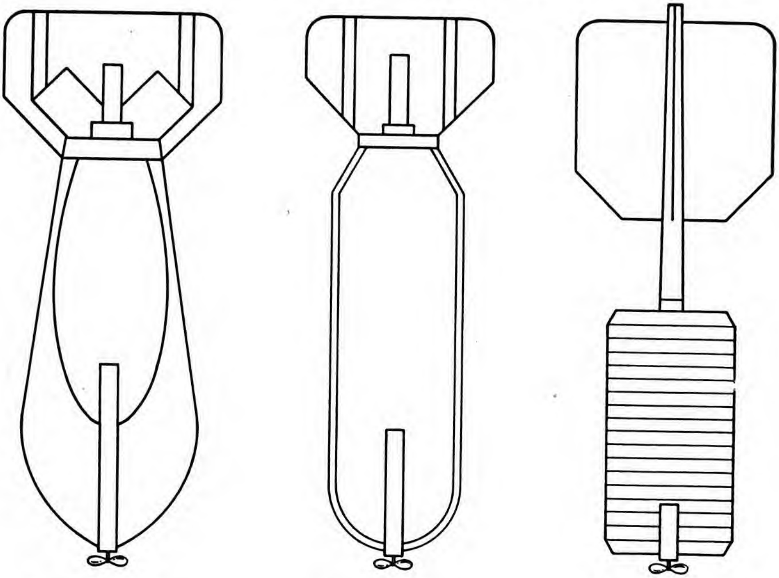
The bomb yields about 40 iron fragments with an effective range of 30 yards, although they may go up to 200.

The percussion mixture in a grenade ignites a black-powder train, which furnishes the delay and may consist of ordinary fuse, and the igniting mixture may fire the main charge either directly or by means of a detonating cap, depending on its nature. The main charge may be 0.74 ounce of E.C. powder, T.N.T., amatol, grenite, or Trojan explosive. Grenades containing high explosive are more dangerous to handle than the E.C. powder grenades, because explosion of one grenade in the packing box may detonate all the others.

Grenades may be made to be fired from rifles by the use of a rod attachment which fits into the bore of the rifle, and the rifle may also have a special cup fitting. Grenades may also be chemical filled.

Bombs for Use by Airplanes. One of the important uses of the airplane in modern war is as a variety of heavy artillery; it has some great advantages over guns. The maximum range of guns is about 30 miles, save for some such exceptions as the "Big Bertha" that shelled Paris in 1918, and the usual range is not over 10 miles. Projectiles in general do not exceed 2,500 pounds at the largest. The airplane is beginning to have ranges up to 4,000 miles one way, a load capacity up to 8 tons and greater which could be all devoted to one projectile if it were so desired. A speed of 300 miles an hour can give a projectile an initial velocity in a horizontal direction of 450 feet per second, which in a fall from any considerable height will rapidly be greatly accelerated by gravity despite air resistance. While shells might be used as airplane projectiles in a pinch, the conditions of flight require special design for efficiency. In addition to the *bomb case*, which is more or less similar to the shell in general shape, without *bourrelet* or rotating band for which there is no need, aircraft bombs must have some kind of *tail fin* to guide the flight. Moreover, weight distribution in bombs differs from that in shells.

The bomb must be released at a considerable distance from the target, in consideration both of air speed and altitude, and sighting is an important aspect. The bomb travels in a more or less steeply parabolic path and if released horizontally hits the ground at an angle which will be about 60° from 4,000 feet, and about 80° at 20,000. These factors are considerably modified by the construction of the bomb. The speed with which a bomb hits the ground, as well as the penetrating ability, is the resultant of a number of factors, which include not only the shape but also the sectional density, which is the ratio of the weight of the bomb to its cross-sectional area. Speed at impact may vary from 350 feet per second for a poorly designed bomb, as an incendiary, to 1,400 feet per second for a well-designed one. While gravity acts as a constantly accelerating force, air resistance increases with speed, and a given bomb tends to reach a limiting velocity where the two balance, beyond which the speed does not increase with increasing distance of fall. As a rule, 20,000 feet is sufficient to attain the limiting velocity, and the time of fall is in the neighborhood of 35 seconds. The velocity of 1,400 feet per second of a well-designed aerial bomb compares very favorably with that of projectiles shot from cannon. Properly designed and released bombs can have penetrations which compare with shells in all respects. Aerial bombs are rated by weight instead of caliber and offer as large a range of variation in types as and a larger range of sizes than shells.



Armor-piercing Demolition Fragmentation

FIGURE 44: **Aerial Bombs**

The armor-piercing bomb has the same purpose as the similar shell, which the bomb case resembles in design, except that it has a tail fin. To ensure positive action all aerial bombs (except small incendiaries) usually have both nose and tail fuzes which are of different design from those used in shells (see page 365).

The bombs range in size from 200 to 4,000 pounds, perhaps even more. A usual size is 1,100 pounds. Because of their necessarily rugged construction, like the armor-piercing shell, only 10% to 15% of the weight of an armor-piercing bomb is high explosive. The explosive is ammonium picrate with a tetryl booster. In warfare armor-piercing bombs are primarily designed for use against well-protected military targets, but civilian population may experience them as the result of misses.

The demolition bomb is the important type of general-use aerial bomb. It may have a variety of shapes. It may be almost completely cylindrical for most of its length with the pointed ogive at one end, and an attached tail fin of two leaves perpendicular to each other at the other end, or it may taper down to a point at the rear with fins attached to the sides of the body at the rear end with a spread only slightly greater than the diameter of the bomb. It may range in size up to 8,000 pounds or more, a usual size being around 500. Such a bomb has good penetrating power, and is used against both military and civilian objectives, except where the maximum of penetration is desired. The usual explosive charge is T.N.T. for the smaller sizes, but amatol or any other explosive may be used, and a tetryl booster is employed. A demolition bomb is relatively thin-walled, and about 50% of its weight is explosive charge.

One unusual form of demolition bomb is the aerial mine. This has been used by Germany. It consists of a thin-walled steel sphere of whose total weight (1,000 to 5,000 pounds) 90% is high explosive. It is dropped with a parachute attached so that it falls very slowly, and has no penetrating power whatever, but as it is used in large sizes, its blast effect is tremendous, and it is very effective. It is fuzed by a number of fuzes about its surface which are of the contact instantaneous type and are very sensitive. Any explosive may be used.

Fragmentation bombs are of generally cylindrical shape. The steel case is corrugated lengthwise and circumferentially so that the bomb will burst into pieces of effective size and weight, which may be 0.2 to 0.3 ounce. It is important in this type of bomb that it explode in a nearly vertical position to give good distribution of fragments. This requires a distinctive design, readily recognized by the square tail fin mounted on a rod which projects from the rear of the bomb, which rod contains the tail fuze. Fragmentation bombs run smaller in size than the others, 30 pounds being typical, but they range from 17 to 2,000 pounds. The principal function of the explosive charge is to propel the fragments effectively and it consists of about 15% of the weight of the bomb.

The fragmentation bomb is fuzed with a contact fuze, and the charge may be E.C. powder, or any propellent explosive, to accelerate the fragments. For use against personnel a 0.2-ounce fragment with 60 foot-pounds of energy is sufficient to penetrate a $\frac{3}{4}$-inch spruce board, and is effective.

Incendiary bombs have been previously described (page 52). The thermite, electron, or magnesium incendiary varies in size from 2 to 60 pounds. The Japanese use a large incendiary filled only with thermite.

Incendiaries of the oil type range in size from 17 to 500 pounds or more, are shaped much like the tapered type of demolition bomb, and contain an explosive charge sufficient to burst the bomb and scatter the contents. Incendiaries of the magnesium type sometimes have explosive charges in a part of each lot of bombs dropped, to excite fear of the bombs and discourage attempts to extinguish them. The use of these seems recently to have become general. Incendiaries of the oil type are usually too large to be successfully combatted by individuals.

Chemical bombs contain gases or smoke mixtures as the main charge, along with a bursting charge of high explosive. Some look like magnesium incendiary bombs in shape; some look also like the tapered type of demolition bomb. They range in weight from 30 to 600 pounds of which about 80% is charge.

Miscellaneous Bombs. Many military explosive devices of the general nature of bombs, sometimes very large, are designed for special purposes.

The depth bomb is designed to sink and explode at a desired depth, for use against submarines. It consists of a large cylindrical metal container which looks much like an ashcan; hence the persisting colloquial term for them. These bombs may contain 1,000 pounds or more of explosive, and are actuated by a type of fuze which operates by water pressure and may be adjusted to any desired depth. Compressed pyrocellulose with a booster charge may be the depth-bomb explosive.

Different types of depth bombs are designed for use by ships and airplanes against submarines.

The marine torpedo is a large, complex cylindrical affair, the major portion of which contains the machinery which propels it through the water. The nose and front end of the cylinder (known as the war head) is detachable, and contains the explosive charge. The torpedo, with war head attached, is fired from a torpedo tube by compressed air or by a small charge of a few pounds of black powder. Once the torpedo is ejected from the tube it supplies its own motive power. The high-explosive charge in the war head may be any of the usual military high explosives, with a booster, and is nose-fuzed with any desired type of fuze, usually contact.

Bomb Testing. Many types of tests are performed upon bombs and explosive devices, falling under the general headings of functioning, trajectory, and safety tests. These are performed in the field and the chemist has little to do with them, although his work has primarily determined the characteristics of operation. In general, the tests determine whether the bomb can be dropped safely, that is, without detonation on impact; whether the case will withstand crushing; whether the magnitude of blast and fragment effects of the bomb are satisfactory; the extent and character of fragmentation; the actual effectiveness against specific targets; the actual effectiveness in causing casualties, by tests on man-sized panels at specific distances; crater formation; other characteristics suitable to the specific purpose of the bomb.

Use of Military Explosive Devices. Since, in the main, these devices are to be used by people who know little or nothing about their contents, construction, or operation, beyond the practical things which they must do to use them, all military explosive devices bear characteristic markings stenciled and painted in color upon them, which convey certain types of useful information, and it is important to become familiar with them. This information can be obtained from appropriate military manuals.

The task, however, of performing any mechanical operation upon actual military explosive devices is one which should never be attempted, until one has had training in handling the devices themselves. Even after thorough training, the task of handling those which have failed to work under prescribed conditions, due to faulty fuzes and other causes, and duds or unexploded bombs (UXB's), is a highly perilous one, and as a rule army regulations prescribe destruction under fixed conditions, rather than any attempts to repair. In any event these tasks are for specialists who are usually military, though sometimes civilian.

The Materials of Construction of the Military Devices. Military ammunition, apart from explosives, represents a large and diversified use of metal. Cartridges have brass or copper cases; steel cases are a recent innovation. Balls in general are lead-antimony alloy with or without gilding metal, cupronickel, or steel jackets. Armor-piercing balls have a tungsten-chromium steel alloy core.

Shells, especially of the armor-piercing type, must be carefully designed and constructed of high-quality metal. Armor-piercing shells are made from high carbon nickel-chrome steel; other shells may be plain carbon or alloy steels. The rotating band is of copper or gilding metal, and brass and bronze enter into some of the fittings.

Bombs, other than airplane armor-piercing types and marine torpedoes, do not require such high-quality metal. Cast iron or spun tubing will often do for casings; tail fins are lightly made and usually detachable. Fuzes, however, always require very careful construction.

Discussion Questions and Exercises

1. Make a careful drawing to scale of any explosive device; determine the number and nature of the parts, and the explosives and other materials used.
2. Name the principal operations in loading a large cannon.
3. Tabulate the explosive devices of this chapter with the explosives used in them.
4. Name and describe the three methods of loading large explosive devices.
5. Neglecting air resistance, what velocity should a bomb acquire in falling 20,000 feet?
6. Describe the usual types of aerial bombs.
7. Air-raid precautions usually direct one to lie flat on the ground for protection against fragments. Assuming that in a bomb the principal force acts perpendicularly to the wall at any point, show the probable

distribution of fragments. If a shell explodes in a perpendicular position on contact does the precaution help much?

8. Report on the effects of the various military explosive devices.

9. Assuming that it takes about 30 pounds per acre to lay an effective gas attack, determine the number of aerial bombs of any given weight and the number of airplanes necessary to carry them, to cover an appreciable area of New York City (total area 300 square miles).

10. Report on the testing of aerial bombs.

CHAPTER 15

Practical Initiating Devices

The General Problem. The practical problem of firing an explosive makes use of a device the essence of which is an initiating material of the types we have discussed and suitable for the task in hand, but the device itself may either be simple or be complicated by various mechanical aids to the process. Such devices are known by a variety of names: fuses, fuzes, igniters, initiators, primers and detonators, and as popularly employed, while they do the job in question, the name is not always closely descriptive of the function. The term primer should be used in the sense of a mechanical device, containing a reasonably sensitive explosive designed to initiate another explosive by ignition. A detonator is properly regarded as a completely assembled mechanical unit containing explosives designed to induce detonation in another explosive; the blasting cap is a commercial detonator. An igniter is usually a device designed to inflame another explosive, that is, induce explosion by heat or flame, but sometimes the chemical material is loosely referred to as an igniter. Initiator (see page 289) usually refers to an explosive or explosive mixture, but is often used in reference to a mechanical device. Other specific definitions have been given in other places.

The initiating device has two important aspects of operation. One aspect is its reaction to an impulse supplied by the operator. The impulse may be a flame; it may be a mechanical shock—usually supplied by an intermediate mechanical device such as the trigger mechanism of a weapon or the lanyard of a gun or by the contact of a projectile with an object; it may be an electric current. In any case the motion required of the operator is a relatively simple one. The other aspect is the reaction of the device upon the main charge; the reaction must be of such nature as is suitable to fire the charge. The factor of time also enters into the problem, in that it may be desirable either to have the two activating impulses follow each other as closely as possible or to have a definite time interval, which may be short or long.

The important characteristics of the initiating device, apart from its ability accurately to perform its function, are: cost; safety, in the sense of high improbability of its acting at any time after its attachment to the charge except under the exact circumstances when it should; efficiency; keeping qualities; and positiveness of performance. To obtain the maxima of these qualities often requires apparent complexity of design, although simplicity is desirable.

Safety Fuse. Strictly speaking, the term *fuse* applies to a device which conveys flame to a distance to set off an explosive which can be fired by ignition, and the simplest illustration is the laboratory device of this sort described on page 49, or the fuse of a fireworks device. The term *fuze* means a device, usually in part mechanical, which operates by detonation, but often in usage the distinction is not clear.

Safety fuse, also known as miner's fuse, consists of a train of black powder, enclosed in a cylindrical waterproof wrapping of fibrous or other material. It is usually about a quarter inch in diameter and is sold on reels. In one type, which can be distinguished by the fact that it has a single center thread the powder is in a loose form, and in another the powder is pressed to a semisolid and this has two or more center threads.

Safety fuse can be ignited by a match, although this is difficult in the open, and there are various types of fuse lighters for the purpose. It burns at a constant rate; there are two standard speeds, 120 and 90 seconds per yard—but the rate of burning is affected by pressure (altitude), by conditions of use, by temperature, by deterioration, and the like, and allowance for variation up to 10% must therefore always be made.

Safety fuse can be used alone for firing any explosive charge which can be fired by ignition, as black powder or smokeless powder. Care must be exercised to make sure that the far end of a fuse is in intimate contact with the explosive, and when using it for anything but a loose black-powder charge, it is well to have a little loose black powder also. Pieces of any length can be cut like wire, but care must be used in splicing to get contact between the cores; in the loose type it is easy to lose the core. It is well always to work with fresh ends.

Squibs. A miner's squib is a substitute for fuse for igniting black-powder charges in a drill hole. It consists of a paper tube with a powder charge plugged at one end with wax and with a short paper fuse at the other. In use the wax plug is torn off, the wick is lighted, and the device is inserted in the drill hole where the rocket action of the burning charge propels the squib to the main charge.

Squibs are also made of aluminum or copper capsules similar to blasting caps, containing a black-powder charge, an igniting mixture, and electric wires with a thin resistance wire shunted across the ends in the mixture, the whole sealed in with melted sulphur so that only the wires come out and the device is completely waterproof. There may be a black-powder pellet between the heating element and the ignition charge, to give a delay action for a second or two. Delay units are also made separately, and may be used with blasting caps.

Blasting Caps. The devices heretofore described are igniters, and can be used only for that purpose. The blasting cap is a detonator.

A blasting cap may be a hollow metal cylinder closed at the business end which is also indented with a slight hemispherical hollow (Munroe effect) and is more effective in the direction of its base. It may be about 1½ inches long and ¼ inch in diameter, and be made of aluminum, copper, brass, or gilding metal. Empty blasting-cap shells are useful in the explosives laboratory for making up test detonators, in the heat test, the sand test, and others.

In practice the charge of the blasting cap is all at the closed end and the open end is empty, but it must be remembered that the charge extends some distance up the tube. The charge may be, and formerly was, simply fulminate mixture, of varying weights for the different sizes designated by numbers from 1 to 10. No. 6 is the commonly used size, and now in the United States the only one. No. 8 is the largest usually obtainable. Today the charge usually consists of a base of tetryl (although P.E.T.N. or other explosives may be used), with about 0.3 gram of fulminate mixture on top, and a little pressed black-powder ignition mixture on top of that.

This type of blasting cap is intended to be used in conjunction with safety fuse. A piece of safety fuse is cut with a clean flat end which is inserted into the open end of the cap and pushed down until it presses firmly against the inner charge (Figure 45). Capping and crimping must be done carefully with the cap held away from the body. The cap is then firmly attached to the fuse by crimping with a crimping tool (Figure 46). The circular notch in the jaws fits around the cap, and presses a circular groove in the cap shell which holds it firmly to the fuse. The cap must be crimped as near the open end as possible, and above all, care must be used not to squeeze the charge, which would be fired. A No. 6 cap explodes with the noise and power of a good sized cannon firecracker and must be treated with respect. Crimping can be done with a dull pair of wire-cutter pliers, and workmen frequently use other methods, but these are not desirable and a good rule to start with is always to use proper tools and methods. A good crimp is completely waterproof, particularly the double crimp made by certain types of crimping machines. In use the business end of the blasting cap should be in contact with the main

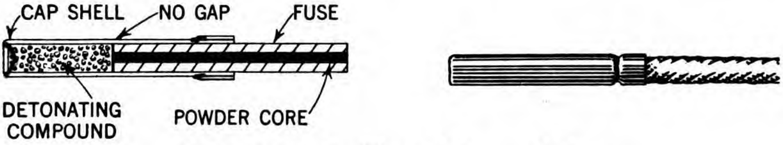
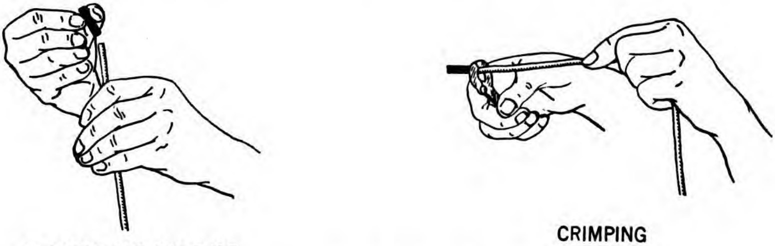


FIGURE 45: **Position of Fuse and Cap**
(Courtesy of Ensign-Bickford Co. and Du Pont Co.)


PLACING CAP ON FUSE

CRIMPING

FIGURE 46: **Crimping Tool and Method of Use**
(Courtesy of Ensign-Bickford Co.)

charge, which it fires by detonation. The fuse is ignited by fire, and should be sufficiently long to allow the operator to escape, although practically it usually turns out to be too long, and without other devices would cause too much delay which may be even more dangerous.

Blasting caps may be electric. In this type, above the detonator charge, there is a loose igniting mixture in which the electric heating element is imbedded (see Figure 47). The lead-in wires run through a plug and the whole is sealed with sulphur so that only the wires extend out of the cap. A variety of materials and methods of initiating may be employed in a final complete assembly. Electric blasting caps, as electric squibs, must be made part of an electric circuit for firing, and require a current ranging from about .5 to 1.5 amperes. There is always a certain very short lag between the closing of the electric circuit and the firing of the charge due to the heating element and this may be of importance in certain types of work, as seismic prospecting. Blasting caps are also made with delay elements so that a series in the same circuit may be made to fire at fixed intervals.

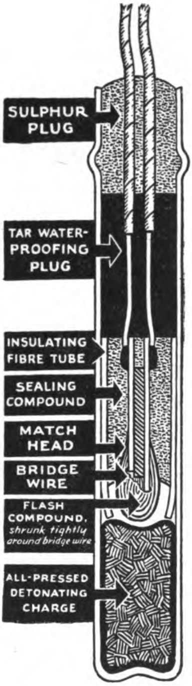


FIGURE 47
Electric Blasting Cap
(Courtesy of Atlas Powder Co.)

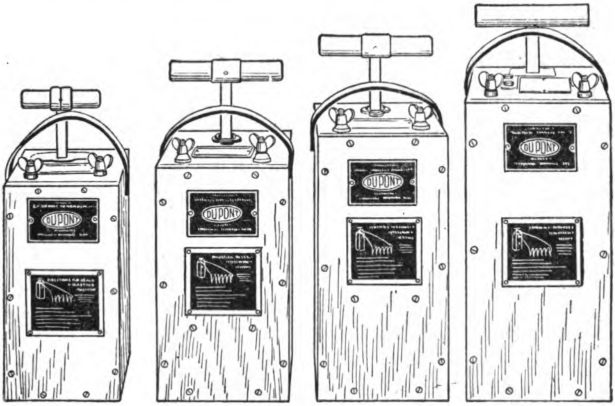
Firing Electric Blasting Caps. Electric blasting caps require electric current to fire. A circuit may be made up with caps in series or parallel or both. The circuit is then tested to determine whether it is complete and to estimate its resistance. The current used here must be very small or there will be danger of firing the charges. This test is often omitted, and all further work is based simply on the number of caps in the circuit.

The source of current may be any convenient battery, perhaps a storage battery, but such a battery usually will not supply current enough to fire more than a few caps simultaneously. It is preferably supplied by a *blasting machine* (Figure 48). This machine, which may be either a magneto or a generator, is hand-operated by means of a downward push or a twist of a bar.

Blasting machines develop 110-300 volts of either alternating or direct current and are rated on the number of caps they will fire in straight series connection, allowing for 30 feet of connector wires per cap; usual sizes are 1, 10, 20, 30, 50, and 100. They may weigh up to 50 pounds, may be rated as permissible (since there is danger that their power may fire gases in a dusty mine), and are usually designed to deliver no power until the activating stroke is completed.

Cordeau-Bickford. Where the length of fuse is large, the delay of safety fuse is too long, and there are varieties of instantaneous fuse, of which Cordeau-Bickford (see page 33) is one. It consists of a lead tube filled with T.N.T. To make this fuse, a lead cylinder is filled with T.N.T. and then drawn down to the same size as safety fuse, when it can be coiled and handled in much the same way. As T.N.T. is a very insensitive explosive it is as safe to handle as a safety fuse.

Cordeau-Bickford must itself be fired by detonation, which is accomplished by joining a fused blasting cap to a square end by means of a thin tubular union which is crimped to the cordeau and held to the blasting cap by several devices, so that cap and cord are maintained in firm contact. The blasting cap may be fired by igniting the fuse as usual. The cap initiates the cordeau by detonation, and in the cordeau the explosion wave travels at about 17,500 feet per second, which is practically instantaneous, so the only delay is for practical purposes, due to the safety fuse, which therefore in a given case may have to be carefully computed.



No. 20 No. 30 No. 50 No. 100

FIGURE 48: **Push-Down Blasting Machines**
(Courtesy of the Du Pont Co.)

Cordeau can be used for initiating explosives which may be fired by detonation, and has many advantages over blasting caps for that purpose. These include greater efficiency and ease of handling. In addition, cordeau has some very ingenious applications alone: stripping bark from trees can be accomplished merely by firing the cordeau looped about the tree.

In using cordeau as an initiator, it is necessary only to tie it around the explosive as one would tie a package with cord, although it may also be laced through holes drilled in the explosive with an appropriate tool. The slight separation due to the casing of the cordeau and the packing of the explosive is not important, although in general no separation should be greater than $\frac{1}{8}$ inch. Initiation takes place at all points of contact and so the effect is far greater than that of one blasting cap.

Cordeau can be spliced by joining two square-cut ends with a coupling. It may be joined at right angles by splitting the leg of the T in half and then spiralling the halves to the right and left along the main line, being careful not to destroy the T.N.T. filling in the process. These operations require appropriate tools for workmanlike performance but in a pinch cordeau can be joined and spliced like electric wire, and with reasonable certainty of operation if the splice is firm.

Cordeau-Bickford, in addition to its practical uses, is an excellent standard to use in the Dautriche method of determining the velocity of explosion (page 33). It is made by the Ensign-Bickford Co., and comes in 1,000-foot reels which, depending on finish, weigh from 84 to 110 pounds.

Primacord. This is another variety of instantaneous fuse similar in principle to Cordeau-Bickford. It consists of a waterproofed textile covering, with an explosive core of P.E.T.N. Like cordeau, it must be fired by detonation with a blasting cap, and is relatively safe as to friction, fire, or ordinary shock. Its explosion wave travels at the rate of 20,350 feet per second which is nearly 20% faster than that of cordeau.

Primacord comes in 500- or 1,000-foot lengths on reels; 1,000 feet weighs about 20 pounds, much less than cordeau. Primacord is used in all respects similarly to cordeau except that in making unions of all kinds, it is never split and is always treated as a wire. Unions must, however, be tied up firm and tight by at least two overlaps. In everyday use, primacord is tending rapidly to replace cordeau, and is made by the same manufacturers (see Figure 49).

Initiators for Weapons and Military Devices. These are known in general as igniters, primers, fuzes, and boosters, and may be incorporated as an integral part of the final device, when they are small and simple, or come separately as individual devices which have to be set up. Integral incorporation is the practice for the small sizes of fixed ammunition and for some of the smaller bombs and grenades; all others use separate units or assemblies.

Primers for Propellent Charges. Primers in general are classified according to the nature of the initial impulse required to operate them, as friction primers, electric primers, percussion primers, and combination percussion-electric primers; or as igniting primers. The basic explosive must be suitable to the initial impulse, but the action of the primer must be to ignite the propelling charge, which for military use is almost always smokeless powder. Because of the ballistic requirement that all of the propelling charge must be ignited as nearly simultaneously as possible, it has not been practically possible to use the flash from the primer alone. It is always necessary to use an igniting charge of black powder with it. This charge may be within the primer, as a separate device, or with the charge. In fixed ammunition a charge of 20 to 330 grains (1.3 to 22 grams) of black powder is combined with the primer. The igniting charge may be in a separate cylindrical igniter to be attached to the primer. In separate-loading ammunition it may, as we have seen (page 318), be in igniter pads attached to the charge, or it may be a core within the charge, and may vary in weight from 3 ounces to 6 pounds.

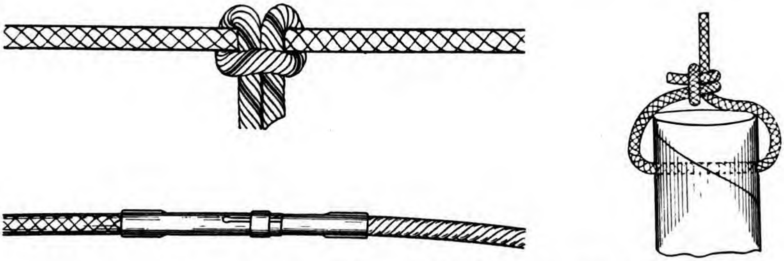


FIGURE 49: **Splicing and Use of Primacord**
(Courtesy of Ensign-Bickford Co.)

The primer fits in the base of the cartridge case or in the firing mechanism of the breech block of a gun, and must be mechanically

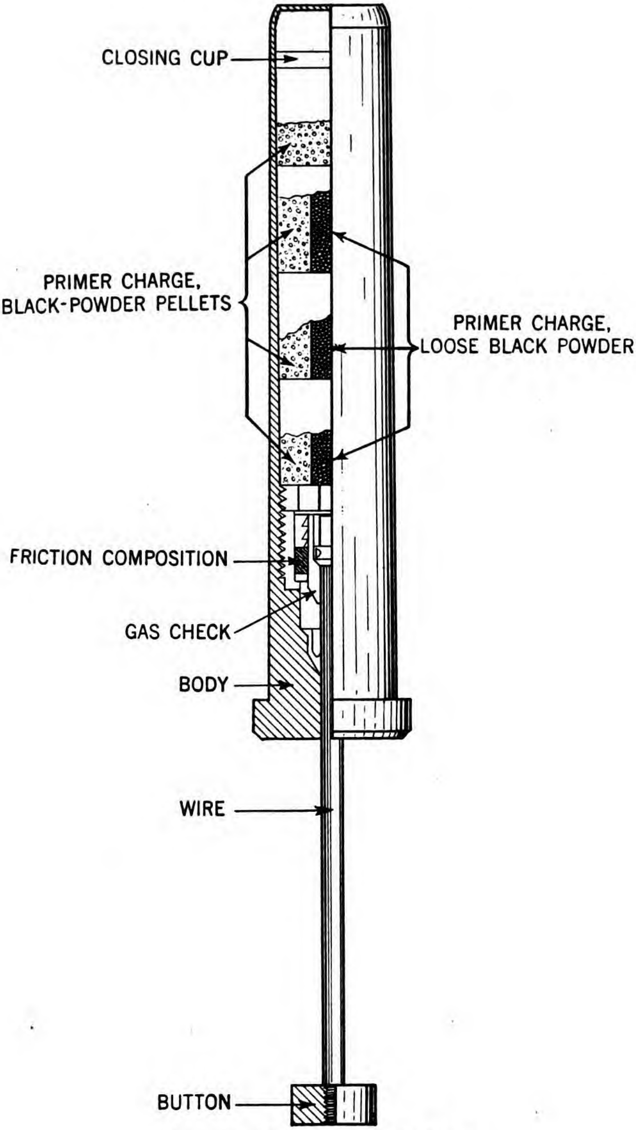


FIGURE 50: **Friction Primer**

tight, and have positive communication of flame to the igniter charge.

Friction Primers. The friction primer (Figure 50) is a metallic cylinder which looks like a cartridge case. A heavy wire, terminating in its outer end in a button, passes through a hole in the base of the

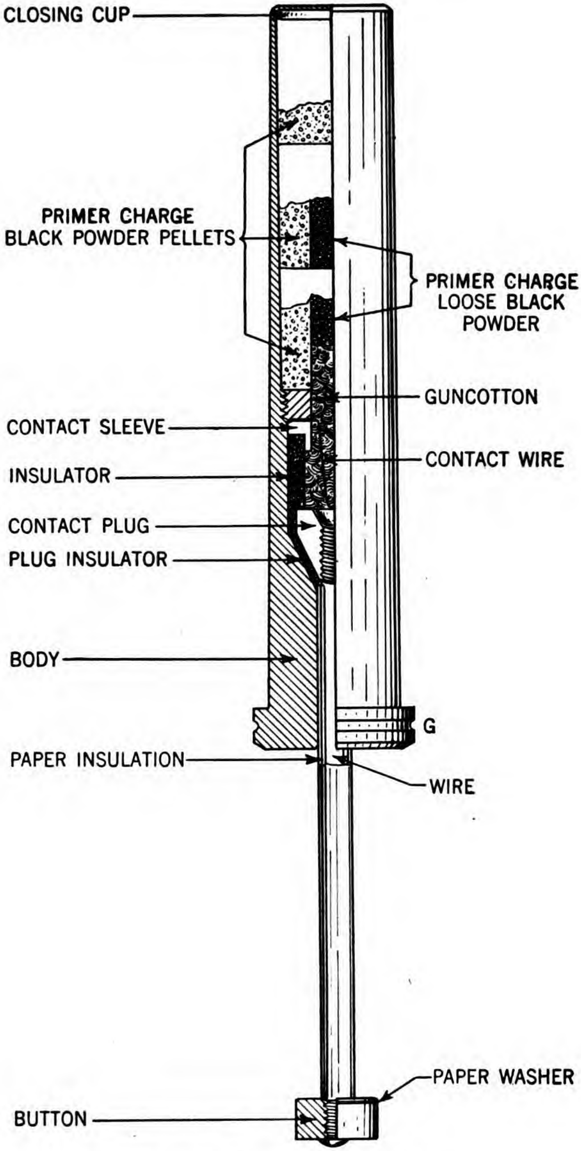


FIGURE 51: **Electric Primer**

primer. The inner wire carries a device which prevents the escape of gases to the rear, and also a metal rod, part of which has teeth to furnish friction when the wire is pulled back.

The breech block of the gun contains a longitudinal hole, the inner end of which should press against the igniter charge. After closing the breech block, the primer is inserted in the hole, and the firing mechanism engages with the button of the primer. A pull of from 30 to 75 pounds must be exerted on the lanyard to fire the primer. The pull of the lanyard closes the cone-shaped gas stop, as it drags the saw teeth over the friction compound. The friction compound is fulminate of mercury, which fires the black-powder igniting charge; its flame in turn is carried through the hole to the igniting charge on the propellent charge. If a primer fails to fire, it is removed and its wire is bent through 180° to prevent its being used again. A steady pull away from the body of the primer should be used during bending, or reverse movement of the teeth on the wire may fire the primer.

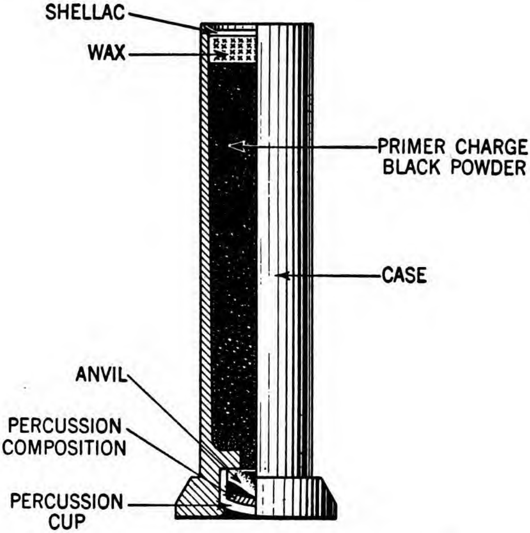


FIGURE 52: **21-Grain Percussion Primer**

Electric Primers. This type is shown in Figure 51. It is similar in appearance to the friction primer except that the outside wire and button is not movable and is one contact of the electric circuit which fires the primer; the other contact is the body of the primer. The primer has an electrical resistance of 3 ohms, and is tested by a mechanism similar in principle to that used in testing a blasting cap circuit. The firing mechanism makes contact with the button, and current of about .5 ampere is furnished by a firing magneto.

The interior explosion train consists of guncotton around the platinum heating element, and an igniting charge of loose black powder and pellets. The expansion of the gases on firing presses the thin walls of the primer against its seat and prevents escape of gases to the rear, and the flame goes forward through the hole in the breech block to fire the igniting charge. The electric primer can be distinguished from the friction primer by a shallow groove machined around the head of the primer body at *G*, which is smooth on the friction primer.

Percussion Primers. These primers are similar in construction to the firing mechanism of a small arms cartridge, except that they are larger and more rugged and have in addition to the percussion mixture, a varying amount of black powder as an igniting charge, and the larger ones have holes in the walls to facilitate the transmission of the flame to the charge.

As shown in Figure 52, the essential parts are the percussion cup, which is struck but must not be perforated by the firing pin; the percussion composition, $Pb(CNS)_2$, or fulminate mixture, which is pressed up against the anvil by the cup and exploded, to communicate its flame to the igniting mixture through holes in the anvil. The percussion cup in all percussion primers, including small-arms cartridges, is sensitive and must be protected against blows having firing-pin action. Such a blow from a 1-pound weight dropped only 3 inches may fire them. Percussion primers have different weights of igniting mixture, and familiar sizes are 20-, 100-, 110-, 300-, and 330-grain. There may be slightly differing internal mechanical features.

Primers are used for the larger sizes of fixed ammunition but in this case are fixed in mechanically tightly at the time of manufacture. Whether used for fixed or separate loading ammunition, the primer case must, in use, be securely held to prevent set back action due to gas pressure, and must be positively sealed by the seat to prevent gas leakage.

Combination Percussion-electric Primers. This primer, shown in Figure 53, combines the two features in a slightly modified mechanical design. When a firing pin is used, the pin acts directly on a plunger in the primer, which squeezes an internal cup and anvil, between which is the percussion composition that communicates its flame to

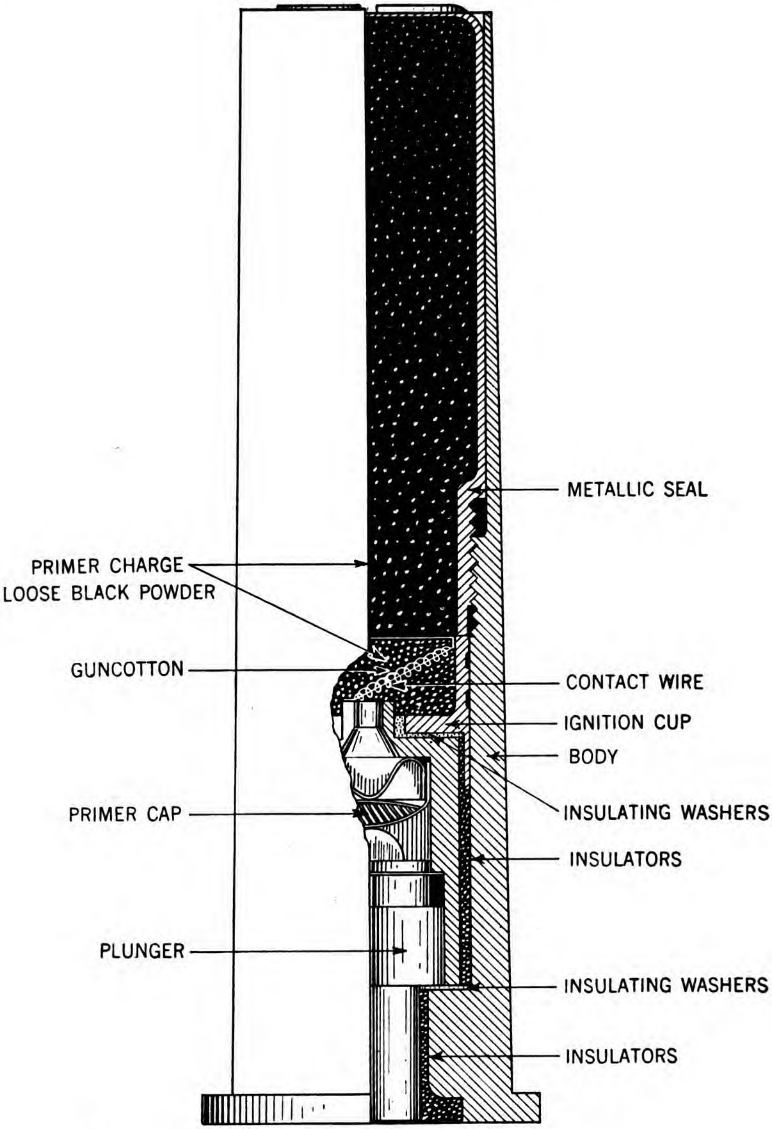


Figure 53: **Combination Percussion-Electric Primer**

a 30-grain loose black-powder charge. When the primer is fired electrically, the plunger and cup mechanism, which is insulated from the case, serves as one contact and the case is the other. The resistance heating element is in the powder charge, surrounded by a little guncotton.

Igniting Primers. These are cylindrical devices which resemble the other primers in appearance, but contain no firing device of any kind, must be used along with one of the other primers, and have internally only 20 or 100 grains of black powder.

Use of Primers. Some of the general types and uses of primers have been described. Primers usually are not marked, and bear on their base only a stamped symbol of the loading plant, lot number, and year of loading. They must be recognized by familiarity.

Fuzes, Boosters, and Adapters. Fuzes and boosters are the devices for firing the bursting charges in all military devices of the projectile type, which usually employ T.N.T., amatol, ammonium picrate, or tetryl, and require detonation. Except in the smaller devices, they are distinct from the device itself, but made in such form that they may be readily integrated with it. An adapter is a mechanical device, usually of the general nature of a metallic sleeve, threaded internally and externally, which may permit a smaller fuze to be attached to a device for which it was not originally designed.

In addition to furnishing detonation, a fuze may also take care of a time element. In the case of a projectile fired from a gun, for example, the bursting charge must not be fired while the projectile is passing through the gun or near the muzzle, but it may be desirable to explode it either at some time during flight, or instantly on contact with any object, or only on contact with heavy objects, or a certain time after contact with an object to allow for penetration of some desired depth, or not until a short or long time after it comes to rest. For bursting charges for military purposes where such considerations are not important, typically in the many military engineering uses, the military man makes use of the devices described earlier for firing, even though the charges are military explosives.

The factor of safety assumes particular importance in the case of fuzes, because military devices contain large quantities of high explosives and their premature explosion is an exceedingly serious accident. Since military explosives are chosen for ruggedness, unfuzed devices are relatively safe. Once fuzed, in the absence of further safety devices, the whole device at once acquires the relatively high sensitivity of the initiator, and a fuzed device can be very dangerous.

Projectile fuzes are designed so that they cannot begin to operate until the projectile has either left the gun (that is, they render the projectile *bore safe*), or is at a safe distance from the discharging device. In addition, the newer service fuzes are *detonator safe*. That implies that there is an interruption between the detonator and the later part of the explosion train, which can be removed only by some mechanical feature of desired operating conditions, so that if the detonator is fired by accident of any kind, except under operating conditions, it will not explode the main charge. A fuze in the detonator-safe or bore-safe condition is said to be *unarmed*. This is its condition when unpacked and when attached initially to the explosive device. At some time during the use of the device, and before reaching its objective, it becomes *armed*, that is, ready to act, and later explodes or fails to explode. All used and unexploded devices should in general be assumed to have "armed" fuzes and therefore to be dangerous to handle, even though this may not be so—failure to arm may be the reason for malfunctioning. The degree of danger may be estimated if one can recognize the type of fuze. The large quantity of detonator required for large devices is always reduced by using a booster charge. The interruption is always between the detonator and the booster.

Principles of Operation of Fuzes. Black powder condensed to high density burns more slowly than at some lower densities, and more uniformly than at the lower densities where it might have the same speed. A pellet of compressed black powder may be included between the initiating explosive and the booster. It will furnish a delay between initiation and detonation equal to its burning time. By using a powder train held in an annular cavity in the interior of the fuze, the length of which from the point of ignition to the detonator may be varied, firing may be set at any desired time after initiation. Some time fuzes employ this device.

To arm a fuse means to arrange all its parts so that they are prepared to act at the proper time. For safety, some mechanical interruption, which can be removed by the proper application of force, is placed between the detonator and the booster in the explosion train. Two forces frequently used in arming, that is in removing the interruption, are "set-back" and centrifugal force. These are important for projectile fuzes. Set-back is the force that will move any object within a projectile, which is free to move, in a direction parallel to its line of travel as the rate of its motion varies. As the projectile accelerates, set-back tends to move such an object backward; as it decelerates, forward. The principal set-backs occur at the start of flight and on contact with a target, but there is some set-back during flight due to changes in velocity. The small changes during flight produce what is known as "creep," and creep may cause bad performance or failure unless provision is made to prevent its action. Such prevention can be accomplished by virtue of the fact that normally it is a smaller force than the principal set-backs.

Centrifugal force results from rotation of the projectile, which varies from 1,300 to 2,000 revolutions per minute in guns, and this force may be used to operate an arming device. The centrifugal force usually acts either to release a safety device, or to turn a firing pin to a position where it can strike a percussion mixture.

Initiation in a fuze may be accomplished by a firing pin operating on a percussion charge. The firing pin is activated by a weight free to move in a groove parallel to the long axis of the projectile and operated by set-back. The weight may carry the firing pin.

Short-delay types of fuzes have the weight located at the back of the groove, and operate on impact set-back, so that the weight moves forward. Fuzes that operate at a given time after launching the projectile on its course have the weight at the front end of the groove with the firing pin pointing to the rear. The weight slides back as the projectile moves forward, fires the percussion mixture, and the powder train begins to burn. At the predetermined time, the main charge is detonated by the action of the detonator (and booster) at the end of the powder train.

Types of Fuzes. Fuzes may be classified in various ways and these descriptions are illustrative but not all-inclusive. Projectile fuzes may be classified according to their position when assembled with the projectile, as *base-detonating* fuzes and *point-detonating* fuzes, depending on whether they are mounted in a prepared seat in the base or the nose of the projectile. They may also be classified, according to their time of functioning, as *impact* or *percussion* fuzes designed to function on hitting the target, and *time* fuzes designed to function at some predetermined time after start of flight.

An important subclassification of impact fuzes is according to action at time of impact. Delay fuzes allow time for penetration of material targets or for obtaining ricochet action. Various lengths of delay are provided but all are relatively short. The pellet in a *short-delay* fuze burns in 0.05 second and in a *long-delay* 0.15 second. They are used in all armor-piercing projectiles to permit complete penetration before bursting. Nondelay fuzes are designed to burst the projectile on a hard surface before complete penetration or ricochet. Superquick fuzes are designed to produce a burst immediately upon impact before any penetration occurs, thus giving a maximum surface effect. They are used against light material targets, barbed wire, and personnel, and in chemical shell to scatter the chemical entirely above ground. Supersensitive fuzes are designed to burst the projectile promptly on impact against a very light target, as an airplane wing.

There are many other types. Small high-explosive devices usually have built-in fuzes, with mechanical safety devices such as the lever in the Mills bomb (page 322), which often are secured by cotter pins or the like until released by the operator. Special fuzes may utilize air pressure or water pressure, as in the depth bombs and other devices. All usually operate by percussion, and employ a percussion mixture, usually fulminate, followed by an appropriate explosion train that ends in a second fulminate detonator if a high explosive is to be fired, and this detonator fires the main charge if it is small, or a booster if the main charge is large. A more completely detailed description of some important fuzes follows.[1]

Base-Detonating Fuzes. Two base-detonating fuzes which are used in the Coast Artillery Corps are the Mark X and the medium caliber Mark V.

The Mark X Fuze. This is the standard delay fuze for major-caliber armor-piercing and deck-piercing projectiles. The fuze is bore-safe and detonator-safe, and future issues of loaded armor-piercing projectiles will have the fuze assembled in place. The plunger and rotor of this fuze arm at 1,300 revolutions per minute, thus making it suitable for use in gun, howitzer, or mortar projectiles.

Figure 54A shows the general details of the fuze and gives the names of the principal parts.

In the bore of the gun, the fuze parts are acted upon by the forces resulting from linear acceleration (set-back) and by the centrifugal forces resulting from rotation. The initial set-back force is greater than the centrifugal force, and is made to lock the rotor in place in the fuze body. The fuze emerges from the bore of the gun still unarmed, no action having taken place. After the projectile has left the muzzle of the gun and linear deceleration begins, the set-back force ceases and the fuze is armed through the action of centrifugal force.

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[1] U. S. A., TM 4–205, *Coast Artillery Ammunition.*

The firing pin in the plunger is normally held in the unarmed position by two pins and springs which, under the action of centrifugal force, move outward, away from the axis of the fuze, and unlock the firing pin which, also as the result of centrifugal force, rotates to the armed position. The rotor, containing the detonator, is also held in the unarmed or safe position by two pins and springs, which release the rotor under the influence of centrifugal force, in a similar manner to the way the plunger is armed. Centrifugal force also rotates the rotor into the armed position. The rotor stop pin serves to stop the rotor in the armed position. In the armed position of the rotor the rotor lock pin aligns with a hole provided in the fuze body and, actuated by centrifugal force, moves partly into this hole, thus locking the rotor in the armed position. The rotor lock-pin lock is provided as an additional lock and moves into its position as a consequence either of air retardation (or creep) in the projectile or else of impact.

On impact, the plunger overcomes the resistance of the restraining spring and the firing pin is driven into the primer, thus exploding it. This explosion ignites the delay pellet, which burns a predetermined time and then explodes the detonator (containing approximately 9 grains of fulminate of mercury), which in turn detonates the booster charge, consisting of about 470 grains of tetryl, and this last in turn fires the explosive charge in the projectile.

The detonator-safe feature in this fuze is contained in the rotor, which carries the detonator out of alignment with the delay pellet and booster until the projectile has left the muzzle of the gun, thereby preventing action of the booster and projectile charge due to premature action of the primer of the detonator.

Medium-caliber fuze, Mark V. This fuze is used in high-explosive base-fuzed shells, for 3-inch, 12-inch, and 14-inch guns, and 12-inch mortars; and in older types of armor-piercing shot and shell for 6-inch, 8-inch, and 10-inch guns. The fuze is bore-safe and detonator-safe.

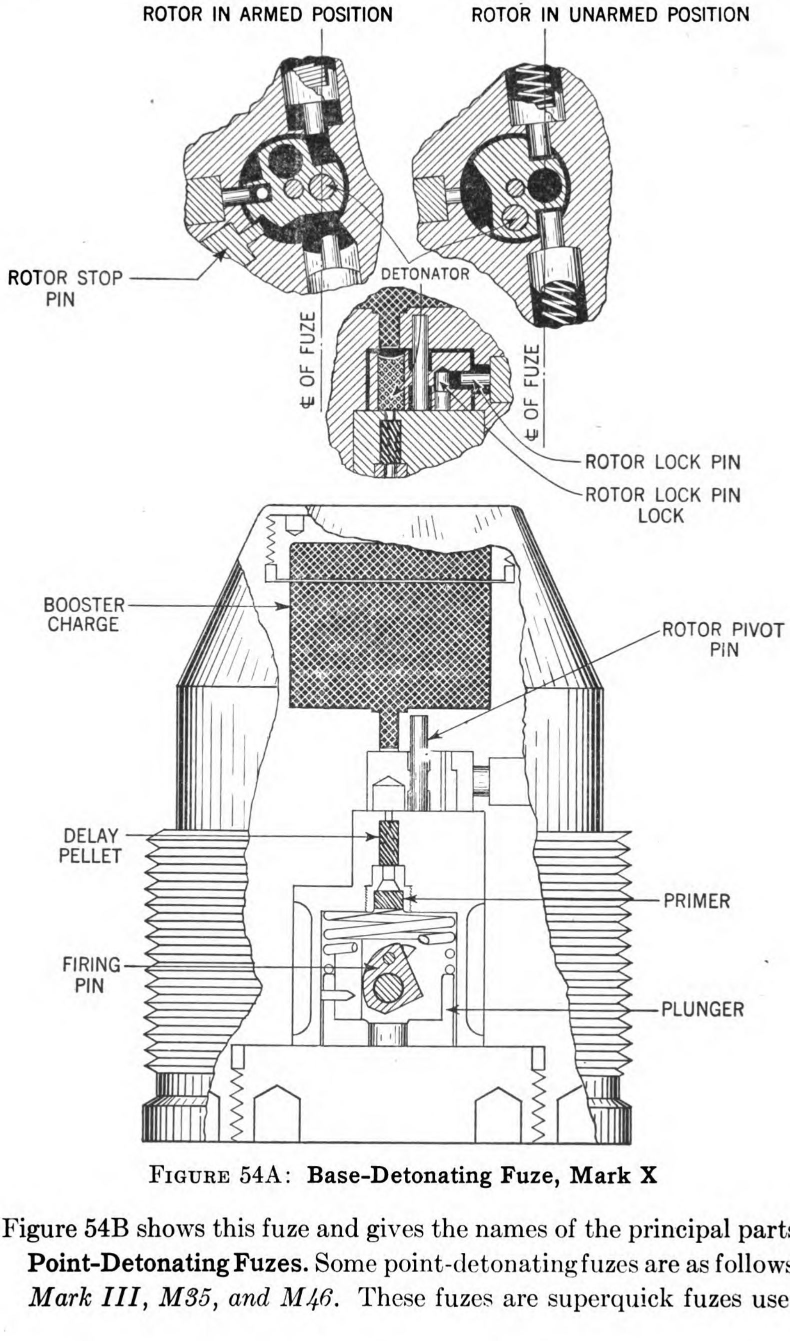

FIGURE 54A: **Base-Detonating Fuze, Mark X**

Figure 54B shows this fuze and gives the names of the principal parts.

Point-Detonating Fuzes. Some point-detonating fuzes are as follows: *Mark III, M35, and M46.* These fuzes are superquick fuzes used

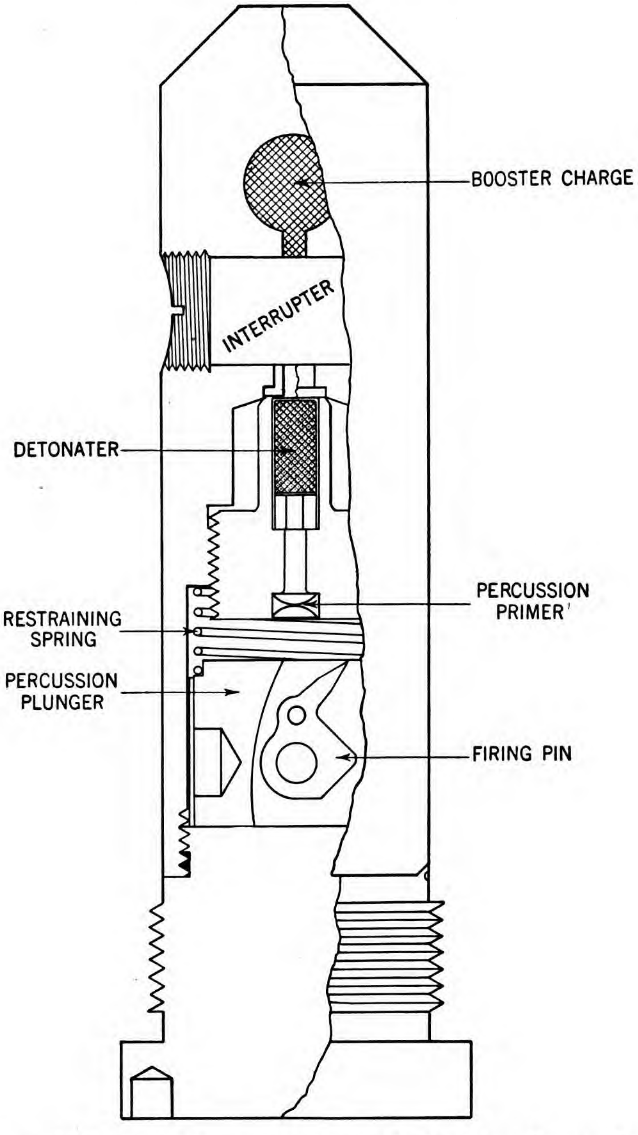

FIGURE 54B: **Base-Detonating Fuze, Mark V (medium caliber)**

when it is desired to secure a quick burst above the ground or target with the least possible penetration by the projectile. Hence they have little or no value for use against naval targets. They are used in coast artillery weapons for fire against land targets. They may be used with 155-millimeter high explosive and chemical shell, and 10-inch and 12-inch point-fuzed high explosive shell. There are many of the Mark III fuzes and some M35 fuzes on hand, and in general either may be used when M46 fuzes are not available. However, many of the Mark III fuzes on hand are being converted to M46 fuzes by modification, and only the M46 is to be manufactured in the future.

Figure 55 shows an M46 fuze, which is the standard fuze of this type. It was developed by improvement of the M35 fuze, which was itself developed by improvement of the Mark III fuze. The M46 fuze is shorter, simpler, safer in handling, has a more powerful detonator, and is much more reliable than the Mark III fuze. The parts labeled on the figure and their functions are described here.

The interrupter constitutes a partial detonator safety device and is operated by centrifugal force. It is set at an angle so that linear acceleration (set-back) tends to oppose the centrifugal force. While the projectile is being accelerated in the bore of the gun, the interrupter remains in the position shown (unarmed) and prevents any premature action of the lower assembly should the detonator assembly function after linear acceleration ceases. Centrifugal force moves the interrupter outward (armed) and clears the flash hole between the two detonator assemblies. The firing-pin assembly is held away from the detonator assembly by the firing-pin support.

When the round is fired, the firing pin support is sufficiently strong to withstand the force exerted on it by the firing-pin assembly on set-back, thus preventing contact of the firing-pin point with the detonator assembly. Upon leaving the muzzle of the gun, rotation caused by the rifling of the bore has created sufficient centrifugal force to throw the interrupter outward against the pressure of the interrupter spring, the restraining forces caused by set-back no longer being effective after the round leaves the muzzle of the gun. The outward movement (arming) of the interrupter opens the passage connecting the detonator assembly and lower detonator assembly.

Upon impact with the target, the closing disk, crimped in at the nose end of the fuze, is punctured and the firing-pin assembly is forced to the bottom of the cavity therefor in the head, collap-

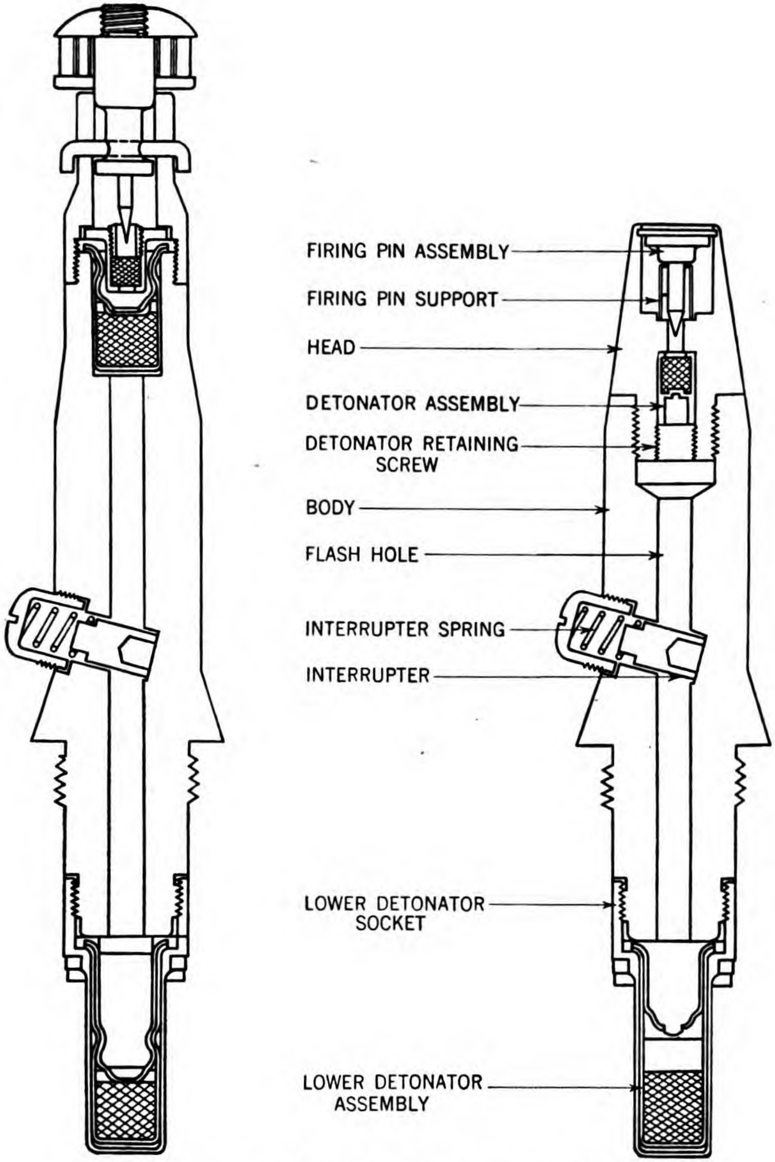

FIGURE 55: **Point-Detonating Fuze, M46**

sing the firing pin support, thus effecting functioning of the detonator assembly. Centrifugal force having armed the interrupter, the flame from the functioning of the detonator assembly is then free to pass rearward and initiate the lower detonator assembly which in turn fires the charge within the projectile.

Mark IV, Mark IV-star, and M47. These fuzes are used when a slight delay action is desired. The Mark IV is made primarily for use in mortars and howitzers (low-muzzle-velocity weapons) only. It may be used with high-explosive point-fuzed shell in 12-inch mortars and in 240-millimeter howitzers.

The Mark IV-star fuze was made primarily for use in guns of comparatively high muzzle velocity and may be used with high-explosive point-fuzed shell in 6-inch, 8-inch, 10-inch, and 12-inch guns.

The M47 fuze is the latest design of delay fuze used in Coast Artillery. It is suitable for use in guns, howitzers, and mortars and will replace the Mark IV and Mark IV-star fuzes.

The Mark IV and Mark IV-star fuzes are exactly alike in every way except that the Mark IV-star fuze has a stronger retard spring. To distinguish the Mark IV-star fuze from the Mark IV fuze the bevel edge of the head of the Mark IV-star fuze is painted green; also, a star is stamped on the head of the Mark IV-star fuze immediately following the mark number. Figure 56 shows the fuze, together with the names of the principal parts.

The following types of Mark IV and Mark IV-star fuzes have been manufactured. The amount of delay is indicated by color markings: (*a*) nondelay (N.D.), white head; (*b*) short-delay (S.D.), approximately 0.05 second, black head; (*c*) long-delay (L.D.), approximately 0.15 second, black head and violet detonator socket. The Mark IV short-delay is the only type of Mark IV fuze now on hand.

The M47 fuze is similar to the M46 fuze except that it has a delay element between the initiating element located in the front end of the fuze and the detonator located in the rear end. The delay element is of a type which can be better controlled to give uniformity of time. The standard delay is 0.05 second, but the fuzes may be loaded to give delays of different lengths, such as 0.075 second, 0.10 second, and 0.15 second.

When Mark IV and Mark IV-star fuzes are in action, the arming casing, through its inertia or set-back at the impulse of the propelling charge, compresses the arming spring. The sides of the arming casing disengage the prongs of the safety casing from the percussion plunger, while the prongs of the arming casing engage the collar on the sides of the percussion plunger. The arming casing is thus held back, exposing the percussion primer and completing the arming of the fuze. The percussion plunger is held from creeping forward during flight—a consideration discussed on page 345—by the retard spring.

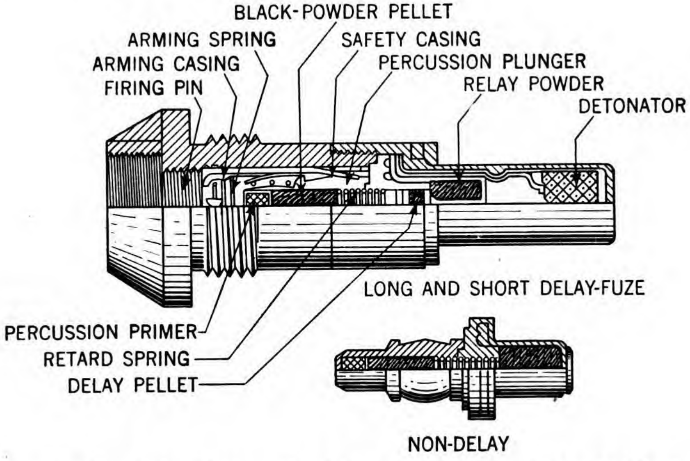

FIGURE 56: **Point-Detonating Fuze, Mark IV and Mark IV-star**

On impact the percussion plunger moves forward, and the primer is exploded by the firing pin. The flame of this explosion is transmitted to the powder pellet below the primer to the delay pellet or to the relay powder in case of the nondelay. The gases from powder pellet are necessary to carry ignition to the relay powder after the delay pellet has burned. The relay powder supplies hot gases which explode the detonator, consisting of approximately 30 grains of mercury fulminate. This fulminate detonates the booster, which in turn detonates the explosive contained in the shell.

The delay pellets are made of compressed black powder, and the pressure of loading and granulation of these pellets is controlled to give the desired delay.

Antiaircraft Fuzes. Antiaircraft fuzes, except those used in small cannon (37-millimeter) (see page 359), must be time fuzes. Direct hits are rare; consequently a percussion element would be of little use. Moreover, the presence of a percussion element is a source of danger in the event that the time elements fail to function, for the projectile would burst on impact with the ground, an undesirable possibility in view of the fact that antiaircraft artillery fire is usually conducted over friendly territory.

Two types of time fuzes are used with antiaircraft ammunition—powder-train time fuzes and mechanical time fuzes. Powder-train time fuzes are not entirely satisfactory for antiaircraft fire, since the rate of burning of the time train varies with temperature and with atmospheric pressure (which in turn vary considerably with altitude), with speed of rotation, and with composition and density of the powder train. The mechanical fuze will eventually replace the powder-train fuze for antiaircraft fire.

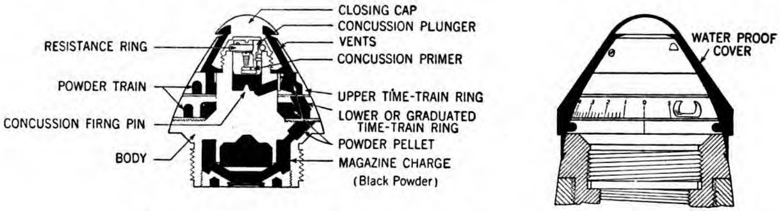

FIGURE 57: **Antiaircraft Time Fuze, Mark III**

Antiaircraft Powder-train Time Fuzes. These fuzes have been used almost exclusively with antiaircraft ammunition during and since the First World War for both the 3-inch and the 75-millimeter antiaircraft guns. The metal parts are made of brass and bronze. The fuzes are always assembled to the projectile for shipment. Each fuze is protected against moisture by a waterproof cover which is removed and thrown away prior to use of the fuze. These fuzes can be set and reset for any time from 0 to 21.2 seconds, the maximum setting; each graduation on the lower time-train ring represents *approximately* one-fifth second of burning time.

21-second, Mark III. Figure 57 (right) shows a view of this fuze with the waterproof fuze cover in place and the fuze set for zero time of burning. It also shows a sectional view of the fuze set at 0 with the names of its principal parts. The heavy magazine charge of black powder in this fuze (95 grains) prohibits its use in conjunction with the booster M20 (see page 364). It is suitable for use with antiaircraft shrapnel, however, although superseded for future manufacture by fuzes of later design.

21-second, Mark IIIA1. This is a redesign of the antiaircraft fuze, Mark III. The principal modification consists of strengthening the nose end of the fuze so that accidental striking of the end of the fuze against the breech of the gun will not make the fuze function. The fuze is similar in all other respects to the Mark III. The Mark IIIA1 fuze is standard for use in all 3-inch antiaircraft shrapnel ammunition and may be used with Mark I and Mark IX high-explosive shells.

21-second, Mark IIIA2. This is an antiaircraft time fuze modified from the Mark IIIA1, the black-powder magazine charge being reduced in weight from 95 to 15 grains. This weight of charge is sufficient to actuate the Mark X and the M20 boosters. The Mark IIIA2 fuze is prescribed for use with all 3-inch antiaircraft high explosive shells.

When the setting is at 0, as shown in Figure 57, the action of the fuze is as follows: When the gun is fired, the concussion plunger slips through the resistance ring, due to inertia or the set-back action in the projectile. The concussion primer, which is held in the concussion plunger, is thus fired by the firing pin. The flame from this primer passes through a hole in the body and ignites the powder pellet, which is in the upper time train ring. The flame from this pellet is transmitted to the ignition pellet, which is located in the lower or graduated time train ring. The flame from this pellet ignites the ignition pellet of the body. The magazine charge in the body is exploded and its flame passes through the central tube to the base charge of the Mark I shrapnel, or to the detonator of the Mark X antiaircraft booster in the Mark I and Mark IX high-explosive shells.

In the above action it is readily seen that when the fuze is set at 0, the action is merely a transmission of flames from the concussion primer to the magazine charge by means of powder pellets. The powder train, which is responsible for the time feature, does not enter into this action. The time fuze, when set at 0, will cause the projectile to burst within 75 feet of the muzzle of the gun.

When the fuze is set for time, 15 seconds for instance, the action is somewhat different. The lower or graduated time-train ring is moved counterclockwise until the 15 is in line with the lines on the body and the upper train ring. The action of the concussion plunger is the same, and the flame reaches the powder pellet as previously described. This powder pellet ignites the powder train. The powder train is machined in both the upper and lower time-train rings in the shape of a horseshoe; that is, there is a solid section of metal at the beginning and end of the powder train. The ignition pellet of the lower or graduated time-train ring has been moved in setting the fuze, and it is necessary that the powder train of the upper time-train shall burn until this pellet is reached by the flame. Then with the ignition of the pellet, the powder train of the lower or graduated time-train ring will begin to burn. After the flame reaches the ignition pellet in the body, the action is as previously described for 0 setting. The gases from the burning of the powder trains escape to the atmosphere by means of the vents in the closing cap.

Every precaution should be taken to keep moisture away from these fuzes. Each fuze is protected by a waterproof cover and the powder trains are covered with waxed paper, but even short exposure in damp places will allow moisture to enter. A piece of felt cloth is on the under side of each powder train to prevent the flame of the burning powder creeping faster than it should. If these pieces of felt cloth get wet, the powder absorbs some of the moisture, which greatly alters the time of burning.

When the lower or graduated time ring is set so that the mark *S* is in line with the lines on the body and the upper time-train ring, the fuze is said to be safe. At this setting, the solid metal section of the upper time-train ring is completely covering the ignition pellet in the lower or graduated time-train ring, and the solid metal section of the lower or graduated time-train ring is completely covering the ignition pellet in the body which connects with the magazine charge. Set at safety, the upper time-train may burn out entirely, in case of accidental firing of the concussion primer, without the flame being able to reach the lower time train or the magazine charge, and therefore the fuze will not function. If not used after making a setting, be sure to remember these fuzes should be reset to "safe" again before handling.

Care needs to be exercised in handling projectiles fuzed with Mark

III time fuze to see that the point is not struck a heavy blow, as this might crush in the closing cap sufficiently to fire the concussion primer and ignite the time train. If the fuze is not set safe at the time, the projectile will burst at the end of the time for which the fuze is set. This carelessness is particularly dangerous when the fuze has been set for a short time of flight.

Accidents of this nature may occur in firing fixed ammunition when a round to be loaded is held in the path of recoil of the gun so that the point of the fuze is struck by the breech as the gun recoils after the previous round. Such accidents become more probable as the rate of fire is increased unless special precautions are taken. When using ammunition with time fuzes, in case the point is struck a heavy blow and the percussion primer is fired, a reasonable procedure to follow is to load the round in the gun and fire it as quickly as possible. If the round is shrapnel a premature burst will not injure the gun. If it is high explosive, it should not be loaded in the gun, but all personnel should instantly take cover.

Mechanical Time Fuzes. This type of fuze is designed to bring about an explosion of the bursting charge of a shell at a more accurately predetermined time after firing than a powder-train time fuze. The time element of the fuze resembles a watch mechanism in general principles, differing from it in the following general respects: Instead of being driven by a main spring, it is driven by a pair of weights which make use of the centrifugal force caused by the rotation of the shell in flight; its escapement differs from that of a watch in that it beats at a very much higher frequency and makes use of a straight escapement spring instead of a spiral hair spring. The advantages of this type fuze are (*a*) greater accuracy of timing than the Mark III type, (*b*) freedom from variation due to atmospheric conditions, (*c*) ability to stand long-time storage without deterioration.

Mechanical time fuze, M43. This model differs from earlier models in external contour and in that it does not contain a booster. The booster used in conjunction with this fuze is known as the M20 and is assembled in the shell as a separate component.

The form and external parts of this fuze are illustrated in Figure **58.** The external parts consist of an upper cap, lower cap, and fuze body.

The upper cap is an aluminum conical frustum, the base end of which is threaded for attachment to the lower cap. It is machined so that a groove is formed in which the fuze-setter locking lever is engaged. This retains the fuze in the fuze setter during the setting operation and prevents the round from being removed from the fuze setter until the proper fuze setting is made. The upper cap does not contain any of the mechanical elements of the fuze.

The lower cap is made of brass. It is slotted for the fuze setter lug and has the usual register line scribed on its surface near the slot. The lower cap forms the cover for the timing mechanism. It is assembled to the body by means of a steel wire which is placed under tension by four small steel setscrews. These setscrews are adjusted in the manufacture of the fuze to obtain the desired tension between the lower cap and the body. They should not be tightened or loosened.

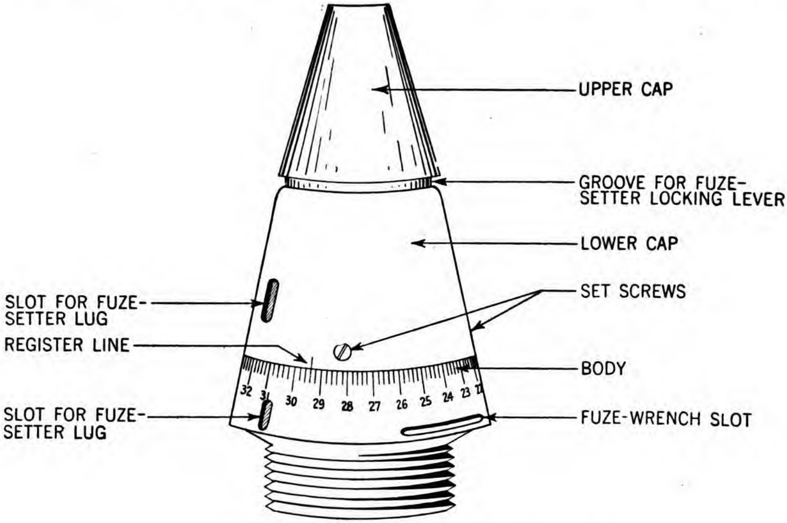

FIGURE 58: **Mechanical Time Fuze, M43**

The body is made of brass or aluminum and houses the timing mechanism. It is slotted for the fuze-setter lug and also contains transverse slots for the fuze wrench. It is graduated from 1 to 30 seconds with $\frac{1}{5}$-second subgraduations. The fuze is shipped set safe with set line on the lower cap in line with the edge of slot in the body. If fired in this position the fuze will not function. When a time setting other than safe is desired, the lower cap is turned in a counterclockwise direction as viewed from above. The body contains a primer which functions the detonator in the M20 booster.[2]

Mechanical time fuze, M2. The action and design of this fuze are very similar to those of the M43 fuze. The principal difference is that the M2 fuze has a booster assembled to the lower portion of the fuze body. It also has a larger thread size than the M43 and is assembled to the 105-millimeter shell, M38, without the use of an adapter. A setscrew extends through the shell wall engaging the threaded portion of the fuze body, locking it in place. The booster of this fuze contains a detonator-safe feature similar to that of the booster M20, described on page 364. The fuze body is graduated for time settings of from 1 to 30 seconds with $\frac{1}{5}$-second subgraduations. A register line is scribed on the surface of the lower cap near one of the fuze-setter slots. This line is set at the 15-second graduation during shipment and storage. For a time setting of more or less than 15 seconds the lower cap is turned in a clockwise direction as viewed from above.

This fuze has been superseded by the M43 fuze and the M20 booster.

Supersensitive Fuzes. Supersensitive fuzes are designed for use with the projectiles fired from small antiaircraft cannon. Such a fuze unit must be so sensitive that it will function promptly on impact with the fabric wing of a plane or with the envelope of a balloon. These fuzes are in process of development and have not yet been standardized. Earlier fuzes are of the balanced-air-pressure type. They depend for safety in flight on the principle that the total air pressure acting on the outside of the striker head is less than the total air pressure acting inside. Air enters the inside through ports in the striker head. When the striker head comes in contact with any object offering any appreciable resistance, the flow of air to the inside is shut off and the outside pressure forces the striker head to the rear. The striker head carries a firing pin which fires the primer and the latter fires the detonator.

The fuze is armed by centrifugal force and is made bore-safe by a locking device in which the set-back force exceeds the centrifugal force until the projectile leaves the muzzle of the gun and linear acceleration ceases. It is made detonator-safe by means of an interrupter carrying a connecting section of the powder train. The interrupter is set at an angle and is operated by centrifugal force, being similar in action to the interrupter in the M46 point detonating fuze.

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[2] A fuze, M43A1, has been designed in which the gripping groove is eliminated, the gripping device having been eliminated from the latest type fuze setter.

The balanced-air-pressure principle has been abandoned, as fuzes built on that principle were not satisfactory. The later supersensitive fuzes are simple percussion fuzes. They also are bore-safe and detonator-safe.

All projectiles fuzed with supersensitive fuzes contain a self-destroying feature, incorporated either in the fuze itself or elsewhere in the round, to eliminate the danger to friendly ground elements from rounds which do not hit the hostile air target.

Marking. Fuzes are identified by markings which are stamped on them by the manufacturer. The information included is as follows: initials or symbols of manufacturer of metal parts; initials or symbol of loading plant; month and year of loading fuze; classification (base-detonating or point-detonating) and mark or model number of fuze; lot number of loaded fuze; amount of delay (in seconds) in case of a base-detonating fuze; point-detonating fuzes are marked S.K. for superquick (head painted white), NoN for nondelay (head painted black), S.D. for short-delay (0.05 second) (head painted black), L.D. for long-delay (0.15 second) (head painted black).

Boosters and Adapters. The function of a booster is to amplify or boost the explosion of the base charge of a fuze to detonate the high-explosive filler of the shell, since the explosion of the base charge of the fuze itself will not suffice. The explosive used for booster charges is usually tetryl (see page 278) or tetryl used in conjunction with T.N.T. Tetryl combines great power and the proper degree of sensitiveness to make it suitable as an intermediate detonating agent.

A booster charge may be incorporated in the fuze itself (as in base-detonating fuzes, Mark V and Mark X) or may be contained in a thin metal casing constituting a unit separate from the fuze.

In chemical shells the function of the booster is to break up the shell and disperse the contents. When so used it is called a *burster*.

An adapter is a metal collar or bushing with internal and external threads, which is screwed into the nose of a projectile. It reduces the size of the opening and provides a seat for the fuze. An opening in the nose of a projectile limited to the size of the threaded portion of a fuze would increase the difficulty of forming and finishing the interior cavity and also the difficulty of filling. The use of different adapters permits the use of certain types of fuze with projectiles of different kinds and calibers.

The booster casing is screwed to the adapter, the two components constituting an assembly known as the adapter and booster. The casing extends down into the bursting charge of the projectile.

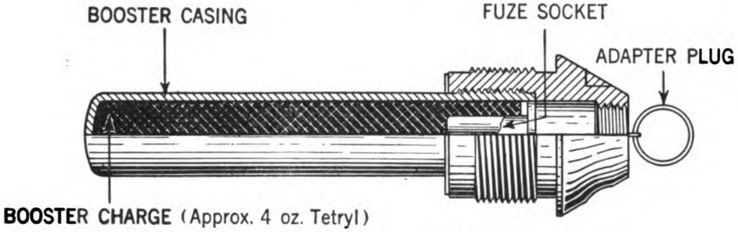

FIGURE 59: **Adapter and Booster, Mark II-A**

Some types of adapters and boosters are as follows:

Adapter and booster, Mark II-A. This model is used in point-fuzed high explosive shells of 6-inch, 8-inch, 240-millimeter, 10-inch, and 12-inch caliber. Figure 59 shows this adapter and booster and gives the names of the principal parts. A fuze socket with a felt or metal plug protects the booster charge from moisture and from the entrance of foreign substances. The booster charge consists of approximately 4 ounces of tetryl. Some boosters are loaded with half tetryl and half T.N.T., the tetryl being placed around the fuze socket.

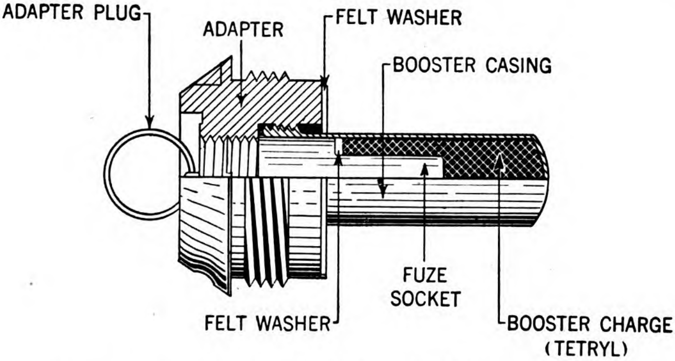

FIGURE 60: **Adapter and Booster, Mark III-A M2**

Adapter and booster, Mark III-A M2. This adapter and booster is used in 155-millimeter high-explosive shell, Mark III. Figure 60 shows this adapter and booster and gives the names of the principal parts. A fuze socket and plug protects the booster charge from moisture. The booster charge consists of approximately 1 ounce of tetryl. Some boosters are loaded with half tetryl and half T.N.T., the tetryl being placed around the fuze socket.

Adapter and booster, Mark VI-B. This assembly is used in 155-millimeter chemical shells, Mark VII. Figure 61 shows this adapter and booster and gives the names of the principal parts. This component differs from that which is used in the high-explosive shell in that the adapter and booster is made in one piece and the threads, by which it is assembled to the shell, are tapered or pipe thread instead of being straight, this type of thread and the one-piece construction being necessary to make a gastight assembly. The joint made by the tapered threads is the only place where gas can escape from the shell due to defective assembly. In view of two facts, first that quite a large booster charge is required to break up the chemical shell, and second that the fuze alone would not dependably detonate this large booster charge, an auxiliary booster is necessary. The auxiliary booster is exactly the same as the booster used in the Mark III-A adapter and booster, the charge being approximately 1 ounce of tetryl. The charge of the main booster is approximately 9 ounces of T.N.T.

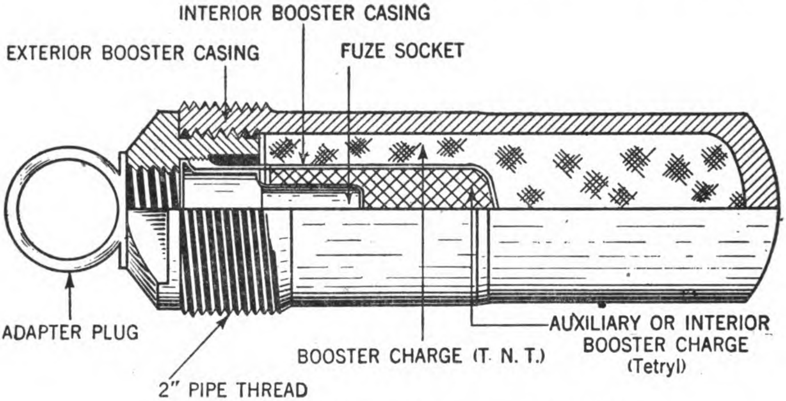

FIGURE 61: **Adapter and Booster, Mark VI-B**

Antiaircraft booster, Mark X. This booster is used in the 3-inch high explosive antiaircraft shell fuzed with the Mark IIIA1 powder-train time fuze. Figure 62 shows this booster and gives the names of the principal parts. Almost all parts of this booster are made of brass. The interrupter constitutes a detonator-safe device, whereby the detonating train is interrupted, between the detonator of the booster and the booster charge, until the projectile has cleared the muzzle of the gun. The interrupter is operated by centrifugal force and is placed at an angle so that the linear acceleration tends to oppose centrifugal force; thus, when the shell is being accelerated in the bore of the gun, this interrupter remains in the unarmed or safe position and prevents any premature action of the detonator from reaching

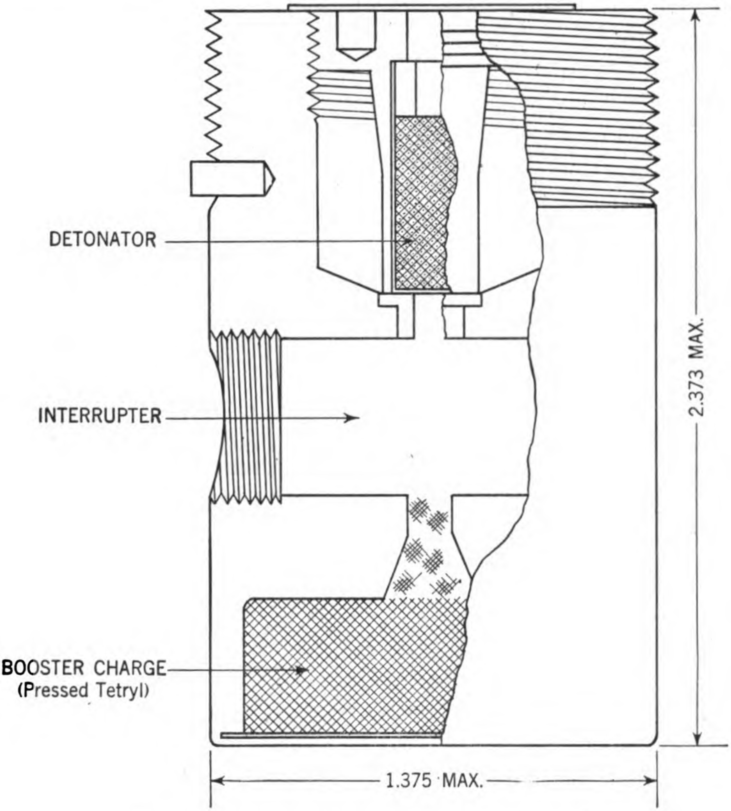

FIGURE 62: **Antiaircraft Booster, Mark X**

the booster charge. After the shell has cleared the muzzle of the gun, linear acceleration ceases and centrifugal force moves the interrupter into the armed position.

When the time fuze has burned its predetermined time, its base charge will explode and fire the detonator, which contains about 12 grains of mercury fulminate. This detonates the high-explosive column leading from the detonator to the booster charge, which in turn detonates the booster charge composed of about 170 grains of pressed tetryl, and the explosive charge of the shell.

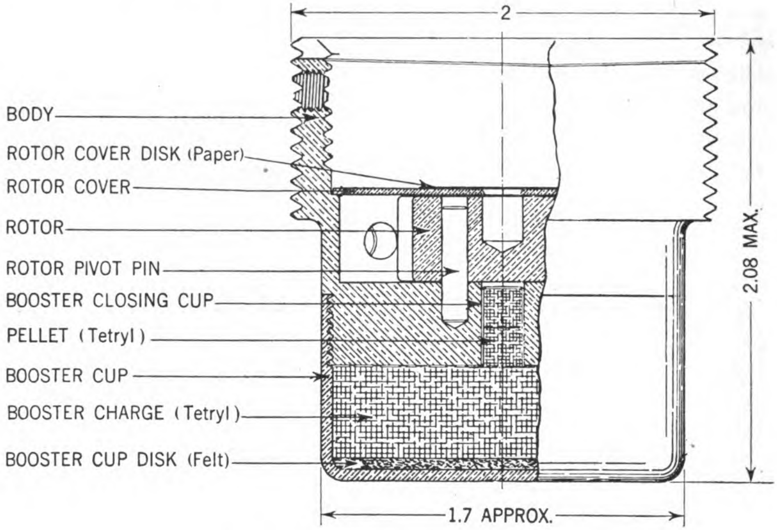

FIGURE 63: **Booster, M20**

Antiaircraft booster, M20. The booster, M20, is used in antiaircraft shell fuzed with M43 fuze or with Mark IIIA2 fuze. Figure 63 shows this booster (rotor in unarmed position) with the names of its principal parts. The detonator-safe feature of this booster is the rotor, which keeps the detonator out of alignment with the tetryl pellet until it is brought in line by the action of centrifugal force. This alignment is not fully accomplished until the projectile has left the bore of the gun. During storage and transportation the rotor is held fast by means of a stop pin which depends on the action of centrifugal force for unlocking.

The detonator, which contains 15 grains of mercury fulminate, is exploded by action of the time fuze. This detonates the booster charge by means of the pressed tetryl pellet. The booster charge in turn serves to detonate the explosive filler of the shell. The booster charge of the M20 booster consists of approximately 420 grains of pressed tetryl.

Conclusion. These fuzes and accessories are described merely as suggestive illustrations. There are many others. Aerial bombs may use some of them but are usually double fuzed, point and base, to make action more certain. The safety device on aerial bombs consists of a rod through the center of the fuze, threaded externally with a small propeller which prevents it from moving. In flight, air pressure revolves the propeller; it runs along the thread, then drops off, and the fuze is armed.

Discussion Questions and Exercises

1. Distinguish between the two initiating impulses of an initiating device.

2. Describe the nature of the two impulses in various explosive devices.

3. Adding a time element, describe suitable explosion trains to serve various purposes in the light of your answers to questions 1 and 2.

4. Describe the construction of: a miner's squib, an electric squib, an electric delay element, an ordinary blasting cap, and an electric blasting cap.

5. Draw a wiring diagram for various ways in which 40 electric blasting caps might be simultaneously fired.

6. How could 40 charges be handled using Primacord?

7. Tabulate the types and uses of primers.

8. Tabulate the types and uses of fuzes described in this chapter.

9. Design a fuze to do some specific job.

10. Tabulate the chemicals of the explosion train of each of the primers and fuzes described in this chapter.

CHAPTER 16

Inspection and Analysis

General Considerations. As elsewhere in chemical industry, inspection and analysis is the field where the chemist finds a particularly important and diversified application of his talents. While much has already been said at other points about these subjects, it will be profitable to review both topics, and there are still a number of important matters to be covered in greater detail. A careful treatment of the subjects should include the details of analysis of all materials and control of all processes related to explosives, also details of procedures for the testing of explosives and explosive devices, and methods for inspection, survey, and testing during the life of the devices. Such detailed consideration would require several volumes the size of this one, and much of the material is not the ordinary work of the chemist. Also it rapidly becomes outmoded, and it is fairly easy to secure up-to-date procedures, if one knows what is wanted.

The general situations in which inspection and analysis become important are manufacturing, purchase and sale, handling, storage, and research. Each of these fields presents its specialized problems, which, however, overlap.

Manufacturing presents the usual chemical problems of analysis of raw materials, process control, and standardization of the product. Analytical procedures for raw materials may be about the same as those used for other purposes, although occasionally the presence of certain types of impurities which would be otherwise unobjectionable become important in producing certain explosives. Traces of nitromethane and other alkyl nitro compounds give poor ratings to smokeless powder and some others in the Abel test, and other impurities have been mentioned. Process control is specialized to the process and involves knowledge of the process, as a primary requirement, and thereafter the usual application of familiar chemical and engineering principles. A number of processes have been presented. Standardization of the product involves general chemical analysis, analysis and testing peculiar to the explosives field, and the effort to correlate operating results with the optimal values disclosed by pure research.

In purchase and sale, testing as a rule must conform to the requirements of a contract, or in the absence of a contract to various standards legal and otherwise. As a large user of explosives of the military type, the United States government has set its standards, which in specific cases cover raw materials and methods of manufacture, sampling, and analysis, storage, packing, and marking. In general, the methods given herein are current United States government specifications, but as standards change from time to time, one should always obtain the current specifications by application to the Ordnance Department of the United States Army. The United States Bureau of Mines and local government agencies have specifications, which are usually legal requirements, with which one must be familiar. These have largely to do with factors related to safety: in use, as in the case of permissible explosives, and in handling and transportation by private and public carriers. Many private users of explosives, sometimes large, do no analytical or testing work whatever and rely entirely upon the statements of the manufacturers. For the products of all of the large manufacturers this reliance is reasonable. Their advertising literature is trustworthy and often amounts to a textbook in the field of the product.

Handling and storage require knowledge of the chemical and analytical behavior of the material, the adoption of procedures based upon such behavior, and periodic inspection by standardized tests, with destruction of deteriorated materials. Here again private users are likely to be careless, especially in respect to explosives in storage. They often make only a desultory effort to use older material first, and aside from so doing take no precautions whatever against deterioration.

General Chemical Analysis. Most practical explosives are mixtures, and the analytic procedure is based upon a knowledge of the approximate intended composition. For a number of explosives the composition has been given. Analytic procedures, from which others may be adapted, have also been given, although for systematic work with ordinary materials it is usually possible to obtain a standard method. Apart from assays of specified chemical components the procedures usually provide for the determination of such components as moisture, residual solvent if solvent, is used, acidity or basicity, insoluble matter, ash, and specific impurities. It is always necessary in practice to make some physical determinations, such as color, form, density, compressibility, and the like. For investigational purposes, the field is still wider.

Most of the important explosives are nitrogen compounds and the determination of total nitrogen is, therefore, an important analytical procedure. The Du Pont nitrometer method (page 232) is specialized and standard for explosives. It is, however, generally applicable only to determination of nitrogen in nitrate esters. One-fourth of the nitrogen in tetryl, the nitro group on the amine, can be determined in this way, and a few other nitro-compounds may be so analyzed. Ammonia nitrogen can be determined by the Kjeldahl method; the method described for determining it in ammonium picrate (page 275) is a modification. The basic method for nitrogen determination in explosives is the usual organic method of Dumas—complete combustion. All the nitrogen procedures may result in explosions when used in this field.

Nitrogen by Combustion: Dumas, or Absolute, Method. This method is based upon the principle of decomposing the organic compound completely by heat and oxidation, absorbing the CO_2 in KOH, and measuring the volume of nitrogen formed. A current of CO_2 is used to sweep the gases through the apparatus. The combustion method is a tedious and cumbersome procedure which requires care, skill, and experience if significant results are to be obtained. The general procedure is an adaptation of the method of Dumas, but microchemical modifications are in much use today. Fisher[1] gives very detailed directions.

The apparatus is set up as shown in Figure 64. It requires three sections of a multiple-unit combustion furnace, shown at *A*, *C*, and *D*, which may be electric, though many chemists still prefer gas furnaces for combustion, believing them to be more easily controlled. The combustion tube should be of good quality and filled with carefully prepared materials. The substance is weighed out into *B*, which may be a porcelain boat. The amount should be about 0.2 gram, or enough to give 15 to 20 cc. of nitrogen. The apparatus is swept out with CO_2. It is well to run a blank determination in advance with a combustible substance that contains no nitrogen, to obtain experience and to see that the apparatus functions properly, in particular that absorption of the generator CO_2 is complete.

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[1] Fisher, *Laboratory Manual of Organic Chemistry*, p. 269 ff.

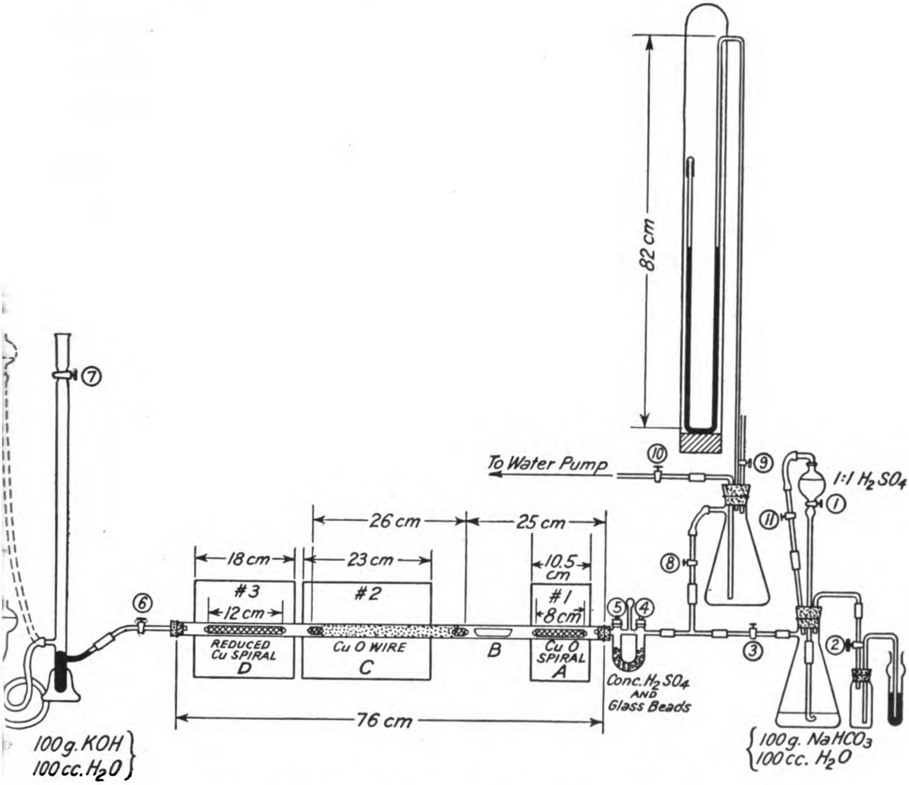

FIGURE 64: **The Dumas, or Absolute, Method of Nitrogen Determination**
(Reprinted by permission from *A Laboratory Manual of Organic Chemistry*, by Harry L. Fisher, Ph.D., published by John Wiley & Sons, Inc.)

In starting an analysis with the apparatus set up from properly prepared materials, as in Fig. 64, disconnect both ends of the combustion tube, remove the copper oxide spiral, and the boat containing the weighed substance to be analyzed, and replace the spiral but not the boat. Reconnect this end only and pass CO_2 rapidly through to drive out the air. Then connect the azotometer at the other end.

Heat only the reduced copper spiral for about 5 minutes, reduce the flow of CO_2 so that it will just keep the gases moving along, and adjust the azotometer so that it is ready to receive nitrogen. None should collect in the azotometer at this time.

If all is well, after allowing the portion of the tube which is to contain the boat to cool to room temperature approximately, disconnect both ends of the combustion tube again, remove the copper oxide spiral, insert the boat and quickly replace the spiral. Proceed as in the last paragraph at this point, and if the results are similar go on from there, as follows.

Turn on heating units (1) and (2) and draw (2) slowly toward the boat, but stop when it is all over the copper oxide and use (1) to heat slowly, and finally strongly, and completely decompose the substance in the boat. This will char and not burn completely in an atmosphere of CO_2, but the process should take about 20 minutes. Allow the CO_2 to pass for about 10 minutes to make sure the nitrogen is all driven over while the furnace is cooling.

Wash the nitrogen in the azotometer with KOH, adjust the pressure, and record volume, temperature, and barometric pressure. Correct the volume for aqueous tension, and calculate the percentage of nitrogen in the sample.

Nitrogen by the Usual Kjeldahl Method. This method is based upon the fact that nitrogen compounds of the substituted ammonia type and some others are completely oxidized to water, carbon dioxide and ammonia by heating with concentrated sulphuric acid in the presence of mercury, copper sulphate, or selenium as a catalyst.

$$R_3N + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4 + \text{oxidation products.}$$

About 1 gram of sample is weighed out, placed in the Kjeldahl flask (see Figure 37) and heated with sulphuric acid and the catalyst. The reaction mixture is diluted with water, and sodium hydroxide or sodium carbonate is added to liberate the ammonia. The ammonia is distilled into an excess volume of a standardized solution of sulphuric acid, which is titrated back with standardized $0.1N$ sodium hydroxide using methyl red or sodium alizarin sulphonate as an indicator.

Kjeldahl apparatus may be obtained as a complete unit, or in series of units, so that the operations are continuous and can be done in large numbers very rapidly.

Determination of Basic Explosive Properties. The basic explosive properties have been described, but they may now be recapitulated with some additional details. The first task of the analyst is the establishment of the explosive reaction or reactions. This is a straight analytical problem to be attacked by a modification of a method applicable to determining the course of any reaction.

This problem has here some special complexity. Where the explosive has an oxygen balance or oxygen excess, the reaction will largely follow an expected course. With an oxygen deficiency, there is, so to speak, competition among the products for the oxygen. Equilibrium will vary according to conditions and the interrelations of a number of reactions, such as

$$\begin{aligned} 2\,C + O_2 &\rightleftharpoons 2\,CO, \\ C + O_2 &\rightleftharpoons CO_2, \\ 2\,H_2 + O_2 &\rightleftharpoons 2\,H_2O, \\ C + CO_2 &\rightleftharpoons 2\,CO, \\ C + H_2O &\rightleftharpoons CO + H_2, \\ CO + 3\,H_2 &\rightleftharpoons CH_4 + H_2O. \end{aligned}$$

As the time of explosion is very short, equilibrium at the explosion temperature will not be completely attained, and the composition of the gases after cooling is not necessarily the same even if it were. The firing of the explosive may be done in a Bichel gauge (page 397).

The heat of explosion may be calculated or determined experimentally by the bomb calorimeter. The determination should always be made where required, and will now be described.

Heat of Explosion by the Bomb Calorimeter. The heat of explosion of an explosive may be determined in the usual type of Parr oxygen-bomb calorimeter which is primarily designed for determining heats of combustion, and is shown in Figure 65. The apparatus consists of an insulating jacket (*A*) which holds the calorimeter (*B*). The latter when in use contains water, a mechanical stirrer, a thermometer, and the properly set-up oxygen bomb (*C*). The bomb is arranged to take oxygen under pressure, and to hold the substance, whose heat of combustion is to be measured, as a prepared pellet, which is fired in the oxygen under pressure by an electric spark, the terminals of contact being carried to the outside of the apparatus.

The heat of combustion (H) produces a temperature rise (ΔT) in the calorimeter which is observed. If the heat capacity (H_c) of the apparatus is known, it is obvious that

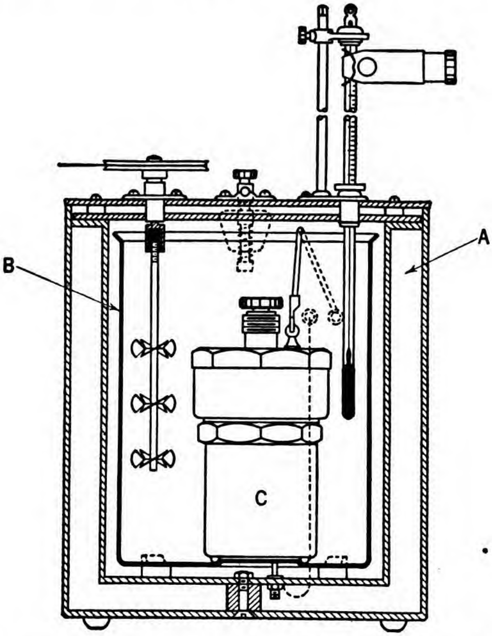

FIGURE 65: **Parr Oxygen-Bomb Calorimeter**
(Courtesy of Will Corporation)

$$\Delta T = \frac{H}{H_c}.$$

H_c may be calculated from the characteristics of the apparatus, or better by using a prepared pellet of a heat standard such as powdered standard coal or benzoic acid to standardize the apparatus.

The heat of explosion of some explosives can be determined in precisely the same way by making pellets of them and firing by the spark. For explosives, no oxygen is used, and the air in the bomb is displaced by nitrogen, since we are not determining a heat of combustion. An explosive which cannot be fired in this way should be made up as a blasting cap (see Sand Test, Chapter 16) to be fired electrically, and a wisp of guncotton can be used over the detonating charge to catch the electric spark, which can be obtained from the inner electric terminals. The cap must be arranged to hang in the bomb so that its blast does not destroy the electric terminals, and it is well to use not more than 0.4 gram of explosive and 0.2 gram of fulminate as a detonator.

The temperature rise will not be as large as usual and the error is correspondingly increased. The bomb must be standardized as before, and a correction determined for the detonating and ignition charge.

Temperature of Explosion. Experimental methods of determining explosion temperatures can be devised in some cases, gas mixtures for instance, but are difficult and unreliable for high explosives with high explosion temperatures, because of the inability of the device to follow the rapid changes in temperature. With few exceptions accepted explosion temperatures are usually inaccurate, probably lower than calculated values and higher than experimental ones.

Explosion Pressures. Explosion pressures can be measured experimentally, as well as calculated. The measurement is usually made with a gauge in which a block of copper or lead is compressed by the explosion pressure, and it is assumed that the effect is the same as the static force necessary to cause the same compression. Such a gauge will measure maximum pressure.

This type of gauge is known as a crusher gauge, and there are two kinds, the fixed crusher and the loose crusher gauges. Both are practical devices. A second type is known in general as the piezoelectric gauge, and is, with the various recording devices of which there are several forms, still essentially a laboratory instrument. It makes use of the change in electrical resistance of tourmaline under pressure, and has automatic recording features that register the rapid changes in pressure occurring during the explosion of a large quantity of explosive in a confined space.

Specifications for propellent explosives for guns usually require, as part of the ballistic specifications, maximal and mean pressures. In practice, these are determined for large guns by inserting a pressure gauge into the powder chamber of the gun, either loose or into a fitting prepared for that purpose. For cannon and smokeless powder, prescribed mean pressures usually are from 9,000 to 32,000 pounds per square inch, and allowable maximal pressures from 18,000 to 40,000 pounds per square inch. 45,000 pounds per square inch is about the highest pressure used in any gun and represents about the present upper limit of construction. For laboratory purposes, pressures may be determined in the Bichel gauge (page 397).

Sensitivity Tests. The heat and drop-weight tests have already been described (page 26). Modifications of the drop-weight test are numerous, using different-sized weights and other modes of impact. Arbitrary sensitivity tests based upon conditions of actual use are valuable. A usual practical test is impact by a bullet from any standard gun at specified distances. Some of these tests are adaptable to explosive devices.

Performance Tests. As has been noted, the physical and chemical tests of properties of explosives are not altogether satisfactory measures of actual performance. Velocity of explosion will indicate in general whether the effect will be propellent or *brisant.* If a propellant is used in a gun, theoretical calculation is in good agreement with actual performance of the projectile. For other uses of low explosives, prediction is not as good.

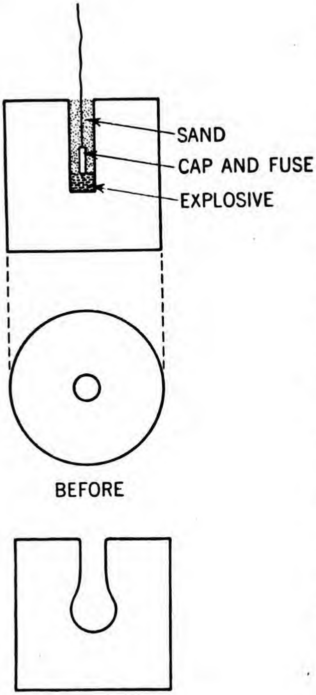

FIGURE 66
Trautzl Block Test
(1/10 size)

For *brisant* explosives there are a number of arbitrary tests which have been named and remain to be described. For a specific task, however, about all that can be done practically is to try the explosive out, and then on the basis of experience set up empirical formulas, which, with the use of numerical factors, will fit several similar explosives.

Experimental Tests. *The Trautzl-block, or lead-block test.* The

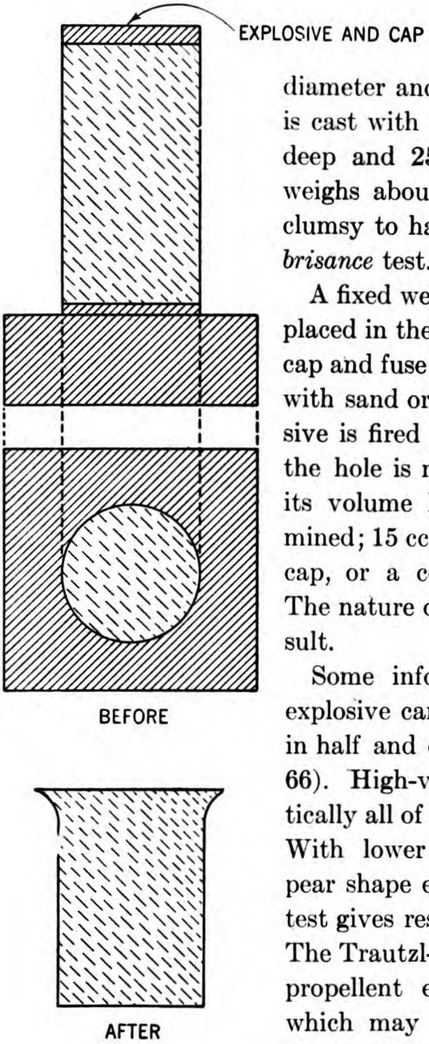

FIGURE 67
Hess Crusher Test
(1/2 size)

Trautzl block is a cylindrical lead block, 200 millimeters in diameter and 200 millimeters in height. It is cast with a central hole 125 millimeters deep and 25 millimeters in diameter and weighs about 80 pounds, which makes it clumsy to handle. The test is essentially a *brisance* test.

A fixed weight of 10 grams of explosive is placed in the hole with a No. 6 detonating cap and fuse attached, and the hole is filled with sand or water for tamping. The explosive is fired and the increase in volume of the hole is measured by filling with water, its volume having previously been determined; 15 cc. is allowed for the action of the cap, or a correction must be determined. The nature of the tamping influences the result.

Some information of the action of the explosive can be gotten by sawing the block in half and examining the hole (see Figure 66). High-velocity explosives show practically all of the enlargement at the bottom. With lower velocities there is a marked pear shape extending toward the top. This test gives results such as those in Table 44. The Trautzl-block test is of little value for propellent explosives, the only action of which may be to expel the tamping, and does not furnish an accurate basis for comparison between high explosives of different velocities.

Hess crusher test, or small lead-block test. This test is also a *brisance* test and may be performed in several ways:

(1) Two lead cylinders 40 millimeters in diameter and 30 millimeters high are placed one above the other resting on an iron or steel

plate. A steel plate 4 millimeters thick and of the same diameter as the lead block is placed on top. From 50 to 100 grams of explosive is placed on the plate and fired untamped.

(2) One lead cylinder 38 millimeters in diameter and 64 millimeters high is placed upon an iron or steel plate. A steel plate 6.4 millimeters thick and of the same diameter as the block is placed on top. Figure 67 shows a steel plate at top and bottom. 100 grams of explosive is fired on the plate without tamping.

TABLE 44

RESULTS OF BRISANCE TESTS

Explosive	Trautzl, cubic centimeters per 10 grams	Hess, millimeters per 100 grams	Sand test, as described, 0.4 gram
Gunpowder	30	0	
Nitroglycerine	590	18.5	
Ammonium nitrate	300	16	
T.N.T.	285		42 g.
Picric acid	300	18–24	
Ammonium picrate	275		
P.E.T.N.	560	22	
Tetryl	320		45 g.
$Hg(ONC)_2$	213		.27 g. initiating T.N.T. >42 g.
$Pb(N_3)_2$			.15 g. initiating tetryl >45 g.
75% guhr dynamite	325	23	

In both of these tests the action of the explosive is estimated by the measured decrease in length of the upper (or only) lead block, and its apparent deformation. Table 44 gives some results. Propellent explosives give no result in this test, and it has the limitations of the previous test.

The ballistic mortar. A mortar mounted as a pendulum is loaded with explosive and fired. The recoil is measured on a scale and referred to T.N.T. or 40% dynamite as a standard. All explosives will give some result here.

The ballistic pendulum. This is a very old test in principle and was originally designed to test the energy of a projectile by receiving it in a pendulum device which would stop it and absorb all its energy. As conducted today the test employs two mortars, one fixed and one mounted as a pendulum. The explosive is fired with tamping in the fixed mortar, and the swinging mortar receives the tamping and measures the result by its swing.

The sand test.[2] United States Army specifications prescribe the use of this test for detonators and boosters, such as fulminate, lead azide, and tetryl. The test is based upon the increase in the degree of granulation of standard sand as the result of explosive action in a bomb. With a standard explosive the test measures efficiency of detonation.

A bomb is properly constructed of iron according to the specifications of Figure 68.

In testing a detonator, .4 gram of T.N.T. or tetryl is used as the standard explosive, with 0.27 gram of fulminate as the detonator, or 0.150 gram of lead azide. In testing tetryl 0.4 gram is used with 0.24 gram of fulminate.

Five empty No. 6 blasting caps (made of copper or gilding metal, 1.46 inches long by 0.217 inch inside diameter) are loaded. The main charge, weighed out, is put in and pressed in a loading block by a plunger 0.20 inch in diameter, which fits into the shell, at a pressure of about 3,000 pounds per square inch for 3 minutes. The weighed detonating charge is put on top of this. A reinforcing cap (outside diameter about 0.217 inch, completely open at one end, and with a hole of 0.11 ± .03 inch diameter at the other end) is inserted with the open end down and a pressure of 3,000 pounds per square inch is applied for 1 minute. By means of a pin, one end of the powder train of a piece of miner's fuse 8 to 9 inches long is pricked; this end is inserted in the loaded cap and seated against the reinforcing cap. Then the blasting cap is crimped, with care to crimp near the mouth of the cap to avoid squeezing the fulminate.

The bomb is to be filled with standard Ottawa sand which passes a No. 20 Bureau of Standards Sand Sieve, and is retained on a No. 30 sand sieve. Into the cavity of the sand bomb 80 grams ± 0.1 gram of sand is poured, and leveled by striking the bomb two or three times. The fuse is inserted through the hole in the cover of the bomb and the cap lowered into the bomb cavity so that it is in the center of the

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[2] Adapted from U. S. A. Specifications for $Pb(N_3)_2$, $Hg(ONC)_2$, tetryl, and others.

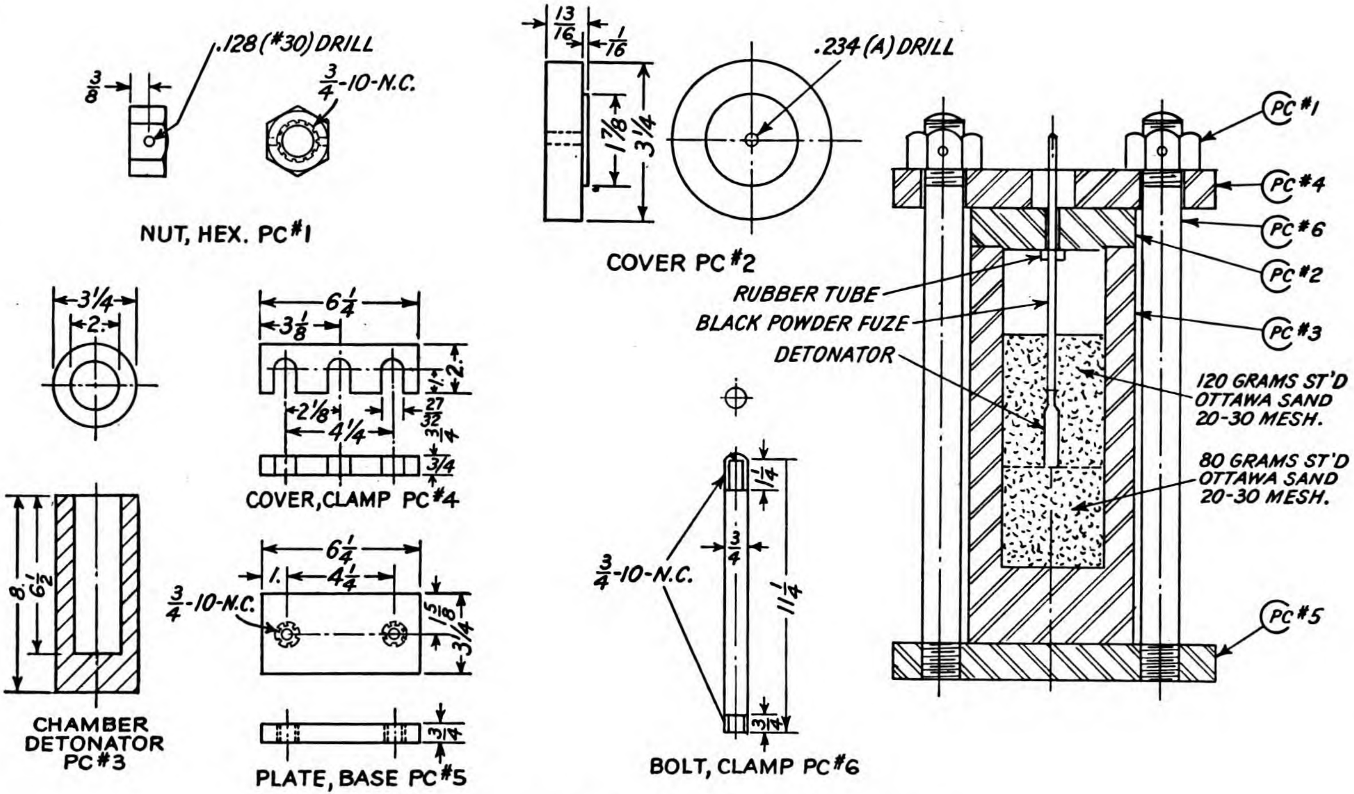

FIGURE 68: **Specifications of Sand-Test Bomb**

cavity and just touching the sand. Around the cap is poured 120 grams ± 0.1 gram more of the sand, and the bomb is tapped as before to level it. To avoid possible loss of the sand caused by the explosion blowing the burned fuse through the cover, a piece of rubber tubing is slipped on the fuse so that the rubber will be against the inner side of the bomb cover when the detonator is in position. It need be only about $\frac{1}{8}$ inch long, and of such diameter that it fits the fuse snugly. The cover is fastened securely to the bomb, with care not to displace the cap in the sand. The fuse is lighted, and after the explosion has occurred, the sand is transferred to a sheet of smooth (glazed) paper, with care to remove any sand which may adhere to the side of the bomb or to pieces of the detonator, shell, or bomb fuse. The sand is put into a No. 30 Bureau of Standards sand sieve, fitted with a pan, and shaken mechanically or by hand for three minutes; then the sand which passes through the sieve is weighed. The average for five trials should conform with the specifications set forth in Table 44.

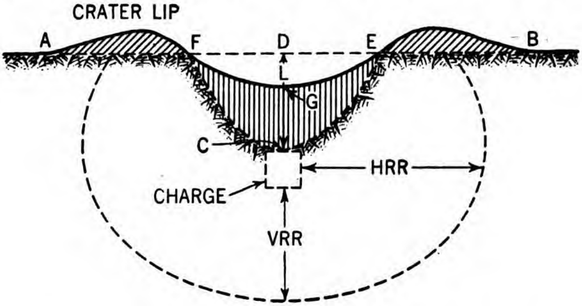

FIGURE 69: **Cross Section of Typical 2-lined Crater**
HRR = horizontal radius of rupture; VRR = vertical radius of rupture.

Practical Performance Tests. These are tests based on employment of the explosive under actual operating conditions and may be illustrated by crater formation. If an explosive is buried deeply in the ground and fired, its pressure will be exerted entirely on the earth about it, and will cause effects for a measurable though variable distance known as the radius of rupture. Size of charge will obviously effect radius of rupture. If the depth of burial is less than the radius of rupture, the explosive will blow through the surface and form a roughly circular depression, known as a crater, at the surface. This state of affairs is pictured in Figure 69. If the depth of burial is much greater than the radius of rupture a cavity will be compressed into the earth known as a camouflet.

In Figure 69, if C is the charge, the ratio of the surface diameter of the crater to the depth of burial ($FE \div L$) determines the nature of the crater. This ratio is equal to 2 for a *common crater*, which is said to be 2-lined. For this type of work a proper charge is one which produces a 2-lined crater; a 3-lined crater represents an overcharge; lower than 2, an undercharge. Based on experience, crater formation can be fairly well predicted by the formula

$$W = \tfrac{1}{2}L^3Z$$

where W = the weight of explosive in pounds; L = the depth in feet to top of charge; and Z = a constant whose value depends on the type of crater to be formed and on the nature of the soil as light earth, common earth, sand, clay, or hardpan—Table 45 gives some values.

TABLE 45

CONSTANTS FOR USE IN FORMULA $W = \frac{1}{2}L^3 Z$

Kind of material	Camouflet, 1-lined	Undercharged, $1\frac{1}{2}$-lined	Common, 2-lined	Overcharged, 3-lined	4-lined	5-lined	6-lined
Light earth	0.010	0.024	0.054	0.162	0.36	0.70	1.23
Common earth	.012	.030	.066	.188	.44	.86	1.51
Hard sand	.014	.038	.084	.252	.56	1.10	1.93
Hardpan or heavy clay (use for roads)	.016	.046	.100	.300	.67	1.30	2.29

After W is calculated, a further amount is added to it, depending on the size of charge, usually as follows: 25 pounds, 100%; from 25 to 100 pounds, 50%; from 100 to 250 pounds, 25%; 250 pounds, 10%.

This formula applies directly to T.N.T., and can be converted, for other explosives, by the use of appropriate factors. It would take about three times as much gunpowder to do the same job. Other characteristics of craters can be computed from similar formulas, and such formulas are available for most of the usual applications. Practical men usually depend upon experience very largely in estimating charges, but there are also nomograph calculators.[3]

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[3] David McCoach III, "Mechanical Computer for Demolition Charges," *J. S. Am. Mil. Eng.*, 33, 446 (1941).

Storage and Keeping Tests. All explosives, and especially the nitrate esters, undergo slow decomposition in storage and keeping which may be accelerated by exceptional climatic conditions of high or low temperatures, extreme changes, or humidity, and by fortuitous access of water and other contaminants. Such deterioration may result in increased sensitivity and in failure to operate under desired conditions. This alteration is often obvious by visual examination to anyone familiar with the appearance of explosives, and is an indication that the material should be removed and destroyed, not used.

As has been seen, explosives are manufactured with a view to improving and maintaining their keeping qualities. The Abel or KI test (page 237) and the heat test (pages 245 and 249), using methyl violet as an indicator for oxides of nitrogen, are used for nitrocellulose and nitroglycerine explosives, and are performed at the time of purchase. The elevated temperatures at which they are carried out, because of the effect of temperature in increasing the rate of chemical reaction, indicate very much longer probable keeping periods in storage. The heat test is conducted at 65.5°C. for straight smokeless powder, at 120°C. for double-base powders, and at 134.5°C. for pyrocotton and E.C. powder. When using these tests on dynamite and other similar explosives, the nitroglycerine is first extracted from the explosive and then tested. If the explosive is tested directly, the fineness of subdivision of the nitroglycerine in the explosive mixture may give a very short test which is not a good indication of its storage properties. Smokeless powder is kept in vacuum boxes which contain strips of $N/10$ methyl violet paper which are changed annually. The appearance of a salmon-pink color at any inspection is an indication of deterioration.

Ballistic Tests. These are usually done with the appropriate weapons on a full scale at proving grounds. The necessary samples, in addition to being representative, must also often be large, and the actual testing is not the usual work of the chemist although it has chemical aspects. Some of the more important tests, which specifications often require, are now described.

Determination of mean and maximal pressures developed within the guns. This test has already been described. It is usually done both for a normal charge and an excess charge of 5%.

Determination of service velocity and velocity uniformity. This test

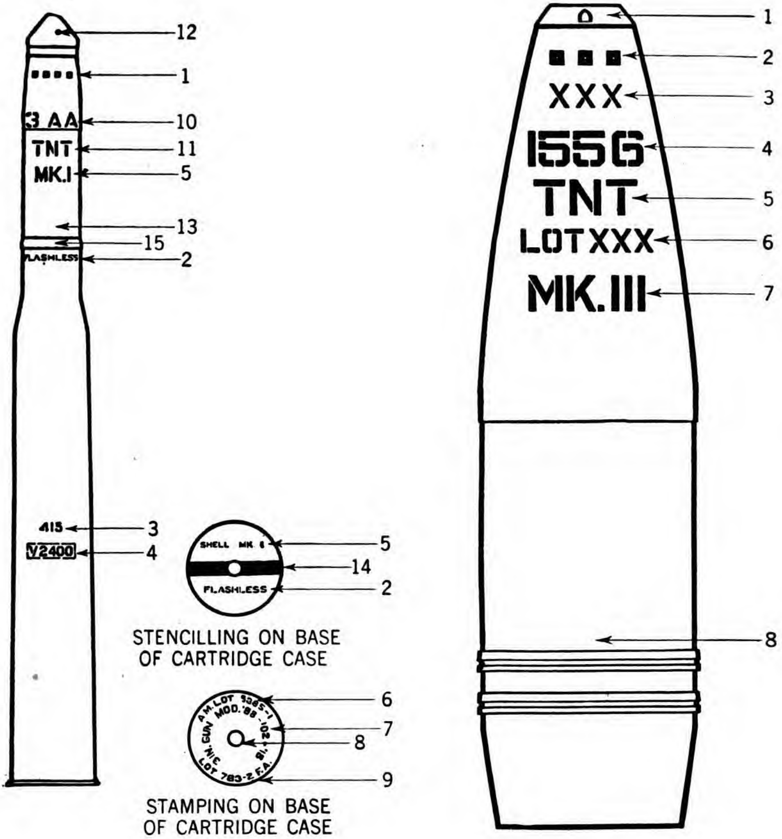


FIGURE 70: **Marking for Ammunition**

Left: Fixed Ammunition for Antiaircraft Guns—(1) weight zone marks; (2) when flashless powder is used; (3) lot number of propelling charge powder; (4) muzzle velocity, in feet per second; (5) mark or model number of projectile; (6) ammunition lot number; (7) caliber and model of cannon; (8) stamping on primer; (9) lot number of cartridge case and initials or symbol of manufacturer of cartridge case; (10) caliber and type of cannon as: 3AA or 105AA; (11) symbol of explosive filler (shell only); (12) fuze and waterproof cover are stamped with model of fuze, lot number, initials or symbol of manufacturer, and month and year of loading; (13) caliber and type of cannon, mark number, lot number of unloaded projectile, initials or symbol of machining plant, and inspection marks (stamped under paint); (14) one stripe as shown denotes service charge; (15) ammunition lot number (stamped on rotating band only when loaded projectiles are shipped unfixed). 1, 6, 7, 8, 9, 12, 13, and 15 are stamped on; others are stenciled in black paint.

is made by firing a prescribed number of rounds with the weapon in question.

The velocity of the projectile is measured, not at the muzzle of the gun, but at a distance from it. The gun is set up so that it will fire its projectile along a known trajectory. Two thin screens are placed in the path of the trajectory at known distances from the gun, usually from 30 to 300 feet for the first one, and the second at a distance of from 150 to 250 feet from the first. The gun is fired, the projectile passes successively through the screens, and the time interval between the two perforations is measured. Distance traveled divided by time gives the velocity. This is known as the instrumental velocity, and the device for measuring the time interval is known as a chronograph.

There are several varieties of chronograph. In the Le Boulengé chronograph the two screens are parts of circuits operating electromagnets which drop rods as the screen is perforated; on one of these rods the time interval is automatically recorded. In the Aberdeen chronograph, the perforation of the screens closes electrical circuits which make a spark record on a spinning drum, after the fashion of the Mettegang recorder (page 33). The solenoid chronograph requires a magnetized projectile, which is fired through a coil of copper wire instead of a screen, thus inducing a current in the copper solenoid which can be recorded in various ways. The instruments are complicated in construction, and each has its field of use. Shells with very sensitive fuses obviously cannot be fired through screens or anything else without exploding. Table 43 summarizes a few of the results required in these tests for some weapons.

Hangfire test. Rifle powders are tested for this fault by regularly

Right (facing page): High-explosive Shell for 155-millimeter Gun, 6-inch Gun, 8-inch Gun or Howitzer, and 240-millimeter Howitzer —(1) adapter may or may not be painted; (2) weight zone marks (⊡ ⊡, ⊡ ⊡ ⊡, etc.); (3) mean or normal weight of shell (unfuzed) in pounds; (4) caliber and type of cannon (G = gun; H = howitzer; GH is the authorized marking for shell interchangeable in gun or howitzer); (5) filler (Initials indicate kind of explosive. May be as shown or AM 50–50 or AM 80–20, for amatol loaded shell); (6) lot number of filled shell; (7) mark number of shell; (8) caliber and type of cannon, mark number of shell, initials or symbol of machining plant, and inspection stamps (stamped on shell under paint). All stenciling is with black paint.

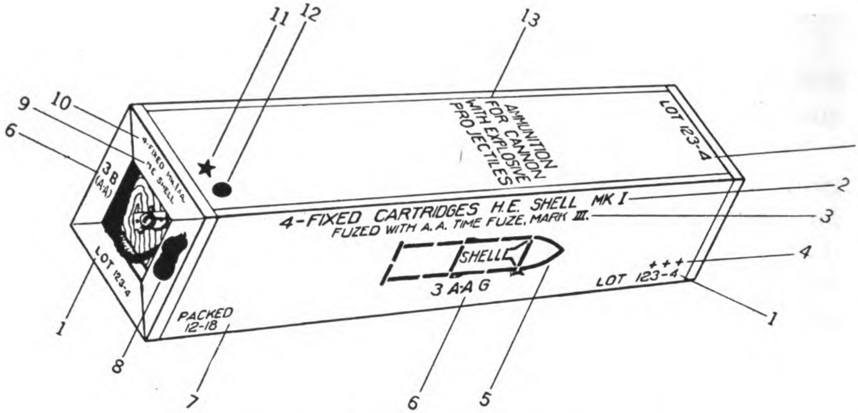
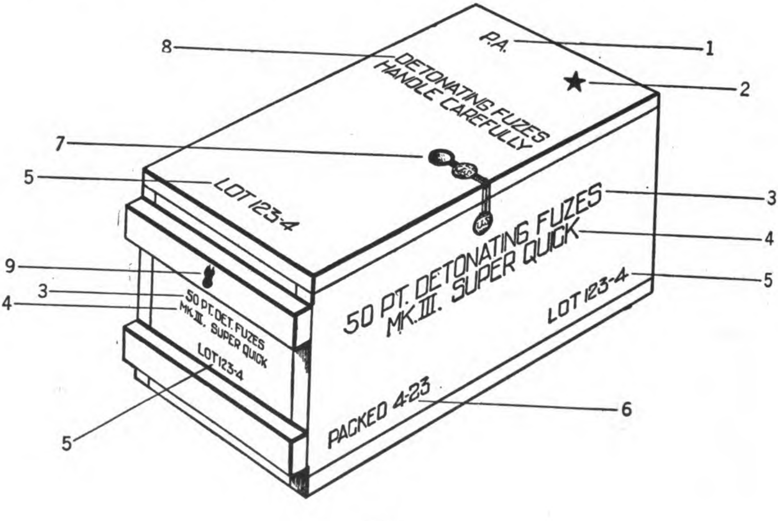


FIGURE 71: **Marking for Packing Boxes**

Above: Packing Box for 3-inch High-Explosive Fixed Ammunition for Antiaircraft Gun—(1) ammunition lot number, (2) number of complete rounds, type and mark number of projectile, (3) statement of fuze used, (4) weight zone marks, (5) symbol of ammunition in box, (6) caliber and type of cannon, (7) month and year of packing, (8) ordnance insignia, (9) type of projectile, (10) number of rounds and mark number of projectile, (11) inspector's stamp, (12) name of place where packed, (13) to comply with I. C. C. regulations. Both ends of box are marked alike.

Below: Packing Box for Point-Detonating Fuzes—(1) name of place where packed, (2) inspector's stamp, (3) quality and kind of fuze, (4) mark number and type of fuze, (5) lot number, (6) month and year of packing, (7) seal, (8) to comply with I. C. C. regulations, (9) ordnace insignia. Both ends of box are marked alike.



and rapidly firing a series of 75 shots at a rotating disk and noting any shots which do not regularly follow the others.

Smokeless test. Rifle powders are tested for this quality by firing 50 rounds with machine gun action at a large white paper target at 150 feet.

Fouling test. Pistol powders are tested for this fault by firing 98 rounds in four minutes from a pistol and then examining the barrel for fouling.

Flashlessness. This is usually determined according to the criterion that the flash shall not be visible by day and be only a dull red glow at night.

The foregoing are tests for propellent powders, and the ammunition required must be assembled from the powder being tested.

Tests of Explosive Devices. These are usually performance tests under operating conditions and have previously been referred to. Adaptations of fundamental tests for explosives are sometimes useful, as, for example, in the sensitivity test of percussion primers by a falling weight. The test described for detonators may be employed for testing blasting caps.

Sampling. No test performed is practically valid unless the method used in obtaining the sample yields one which is representative. The method, therefore, is of great importance and is often part of the specification. The generally important criteria are these. The sample, whether of explosive material or devices, must be representative of the lot. This means that it must be taken completely at random, and samples must be taken from a fairly large percentage of the whole lot. Where the lot is large and is packed in containers, government specifications usually require sampling of 10 containers, and in any event not fewer than 6; where the number of containers is small, all may be sampled.

Ballistic samples and practical-test samples are usually large and necessary chemical samples are relatively small, from 10 to 20 pounds, with much less actually used. They should be taken from the same containers or sources. All products of the first sampling should be carefully protected against contamination, packed in appropriate containers for further protection, and marked so that they can be completely identified if necessary. The original chemical samples should be relatively much larger than is actually necessary.

Original samples are mixed and then reduced in size by quartering or other means of rejection, some of which have been described, to produce the final sample, which is then subjected to the tests prescribed.

Marking. Explosives and explosive devices intended for military use are marked in prescribed and informatory ways which are specific to the object in question. To a degree this is also true of commercial material. For military purposes, numbering, lettering, paint in bands and colors, and other devices indicate such things as manufacturer, date of filling, type of explosive, nature of chemical filler in chemical devices, and many other things. The pictures (Figures 70 and 71) on pages 382 and 384 should be examined carefully.

Discussion Questions and Exercises

1. Review the United States Army specifications for the important military explosives. How do they compare with other large-scale "technical" materials?

2. Report on methods of sampling large quantities of materials for chemical purposes, for example tank-car shipments of liquids.

3. Report on micro nitrogen determination. Report on the paper by Elving and McElroy cited on page 11.

4. Is the heat of explosion of an explosive ever approximately the same as its heat of combustion? Explain.

5. Write equations for the possible course of reaction for all of the explosive materials you know, and calculate the percentage composition of the resulting solid, liquid, and gaseous products.

6. Outline a method for determining experimentally the course of any of the reactions in question 5.

7. Examine the table of results of the *brisance* tests, and draw what conclusions you can from it, and your knowledge.

8. Make up and solve problems using the crater formula, and your knowledge of bombs; for example, assume a 500-pound T.N.T. bomb explodes after penetrating 15 feet.

9. What are the criteria for determining whether a sample is representative or not?

10. How do you account for the difference in behavior of explosives in the Trautzl-block and Hess tests?

CHAPTER 17

Application and Use

Explosives Available. All of the large-scale practical explosives have now been considered to some extent. For general commercial use the commonly employed ones are gunpowder, various kinds of dynamite and blasting gelatin, and explosives which are largely ammonium nitrate such as nitramon. For military use there is somewhat greater variety—the various forms of pyrocellulose, T.N.T., amatol, tetryl, ammonium picrate, picric acid, and nitrostarch. The igniting and detonating explosives come on the commercial market in the form in which they are to be finally used, as squibs, igniters, safety fuse, blasting caps, and instantaneous or detonating fuse. In use, black powder must be fired by ignition; pyrocellulose behaves like a low explosive and gives effects similar to black powder when fired by ignition, but is a powerful high explosive when fired by a detonator; all of the others must be fired by detonators. The nitramon explosives must be fired in conjunction with a special booster charge sold with them, which contains T.N.T. Practical blasters often make use of the booster principle in firing large charges.

Each explosive has properties which fit it peculiarly to certain uses, and in explosive devices this careful relation is used. In general, where a minimum shattering effect is desired, black powder will be employed, although important permissible explosives for mining work belong to the other commercial types. Special conditions of operation, for example under water, often dictate the selection. The practical blaster chooses on the basis of his experience, and, if he is wise, with the assistance of manufacturers' literature which presents more reliable information than is included in most practical experience. For military engineering uses all of the explosives are employed and the distinction between commercial and military is meaningless. Even for other practical purposes, except for maximum efficiency, the usual criterion is availability, since any job, as a rule, can be done somehow with any of them.

Weight of Charge. After selecting the explosive, the next problem is the weight of charge. This is determined by the nature and size of the job. Various formulas and computing methods and devices (see page 380) are available for determining basic weight, but experience is also very valuable not only for quantity but also for placing. Such formulas are usually based upon a standard explosive such as T.N.T. or 40% or 50% straight dynamite, which are practically considered equivalent, taken as 1. Varying weights of other explosives may be employed for the same job, according to an assigned factor which is more or less accurate depending on the nature of the work. This factor for the various explosives is given in Table 46.

TABLE 46

FACTORS FOR INTERCHANGING EXPLOSIVES

Blasting gelatin	2.10
Guncotton (detonated)	1.20
Ammonium nitrate dynamite	1.20
Picric acid	1.06
Ammonal	1.05
Dynamite (15–60%) 50%	1.00
T.N.T.	1.00
Amatol 50–50	1.00
Gelatin dynamite (25–90%) 60%	0.90
Ammonia dynamite (17–60%) 60%	0.90
Nitrostarch	0.90
Gunpowder	0.33

Preparation of the Charge. The charge in correct quantity must then be made up, an appropriate firing device somehow attached, with a fuse of sufficient length to give proper protection to the operator, and the whole placed and fired.

Black powder is often merely poured loose into a borehole and fired by dropping in a lighted miner's squib. High explosives are prepared in granular free-flowing form for pouring into boreholes of such shape or nature that the more usual forms are not easily inserted. A fused blasting cap is then lowered in by means of the connector wires. While complete confinement is not imperative for the action of explosives in quantity, it increases their efficiency and the explosive should be covered by a layer of sand or water (the explosive permitting), known as tamping or stemming. A small surface charge may be covered with earth or plastered with wet mud. These, however, are careless and hazardous methods of use in general.

There are many methods of making up the commercial forms of explosives with the firing device. A few typical examples may be given.

Pellet powder and safety fuse. A piece of safety fuse is gashed in three or four places about 2 inches apart, starting near the end, to expose but not to destroy the core. The end of the fuse is cut on a long bevel. The fuse is pushed through the central channel in the cartridge of pellets, the beveled end turned back so that its cut side contacts the powder, and pulled back so that it holds firmly. When the fuse is lit the powder will be ignited from the gashes in the side, and/or by the beveled end.

An electric igniter is merely laced through the central channel and then brought back and inserted through the top so that it rests about in the center of the cartridge. The wires are then pulled tight. A reasonable pull on the wire will not move the igniter under these circumstances.

Dynamite (or similar) sticks and blasting caps. The dynamite cartridge is opened at one end, and, using a sharp tool, such as the pointed side of the handle of a cap crimper, a hole is punched into the explosive wide enough to admit the detonating cap, and about half again as long, parallel to the long axis of the cartridge. This use is one of the very few exceptions to the general prohibition to using metal tools in contact with explosives. The properly fused blasting cap (see page 332) or electric cap is inserted carefully as far as it will go into the hole, and the wrapper is replaced around the fuse or connecting wires. A stout cord is tied about the fuse or connecting wires at the wrapping, and carried down and tied firmly around the body of the cartridge. This prevents the cap from being drawn out by a pull on the fuse or wires; there are other devices for this same purpose. Another method consists in punching the cartridge through the side obliquely toward the base. The fuse or wires under these circumstances run up the side of the cartridge and can be tied directly to it with loops of cord. Care must be used that the base of the cap does not protrude from the other side of the cartridge, where in loading it might be accidently fired. The largest available blasting cap

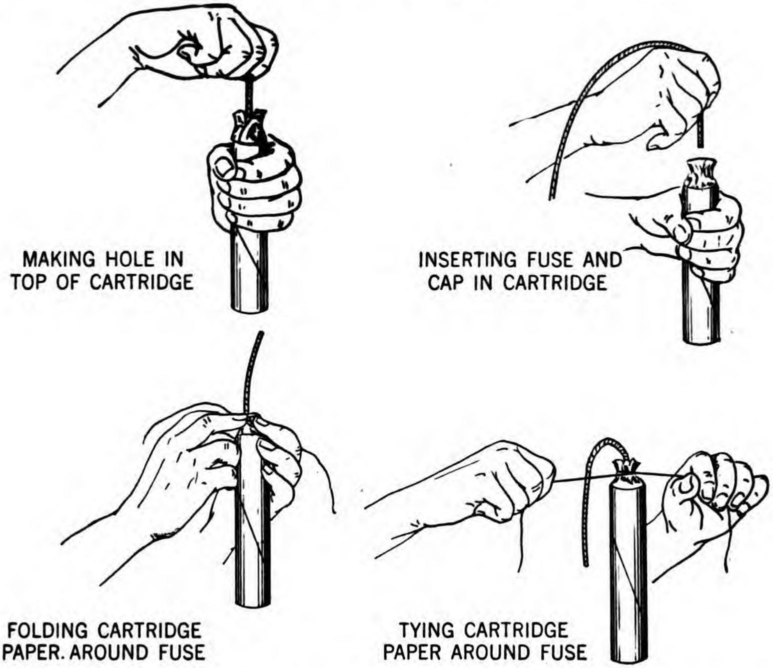
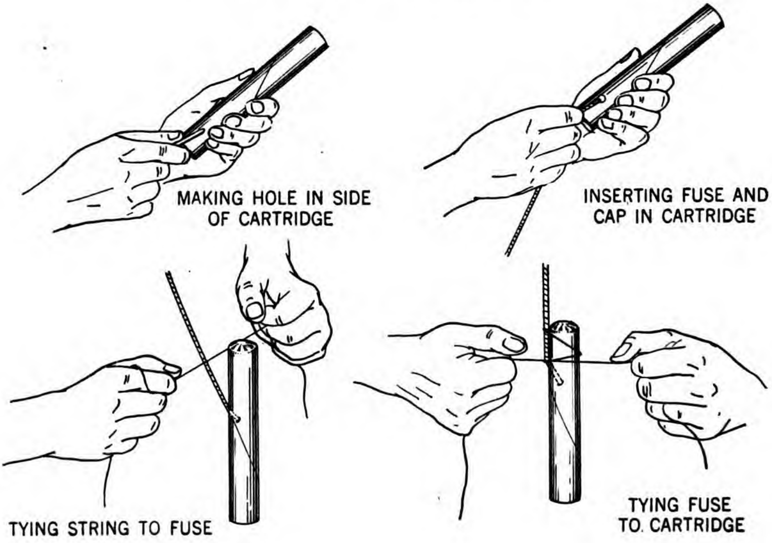


FIGURE 72: **Two Methods of Priming Dynamite Cartridges with Cap and Safety Fuse** (**above and below**)
(Courtesy of Ensign-Bickford Co.)



should be used. A No. 8 is required for efficient operation of the military explosives, and nothing smaller than No. 6 should be used for any.

Block explosives. T.N.T. and similar blocks often have a hole prepared to receive the detonating cap, but if not may be prepared in a manner similar to that for dynamite sticks. In using more than one unit of explosive, as several sticks or blocks, only one unit of the charge need be provided with a detonator, and will detonate all if care is taken to provide good contact, which is important. However, in using large charges it is well to provide at least two detonators to take care against possible failure of one. In filling a drill hole the cartridges are put in one after the other and care must be exercised to see that they make contact. The primed cartridge may be first, last, or in the middle, although under some circumstances one position is desirable over another. With gunpowder the primer is always last in the hole. In making up a bulk charge, the units of explosive should in general be arranged in a symmetrical shape, and tied firmly together with cord or wrapped in paper or sacking. The use of paper or other materials is sometimes discouraged because of the possible formation of fumes. The explosive may often be used in bulk directly in its original packing case. The primer should be in or near the center.

Use of Cordeau-Bickford and Primacord. These may be used in exactly the same fashion, although primacord, in addition to its other advantages, is easier to handle because it is more flexible. Both are detonating agents and obviate the use of caps. For firing, a single cartridge may be punched through by a hole parallel to the end and about 1½ inches from the end, the cord laced through and tied back against itself (see page 337). This may also be used as the primed cartridge of a charge. Or the cartridge may be punched through from end to end, and strung on the cord with a knot tied at the end of the cord to keep the cartridge from falling off. Nitramon and some other commercial explosives are packed in containers having a groove up the side to receive the cord. In firing a bulk charge of explosive, primacord may be used to tie up the package and will detonate at all points where it is close to the package.

Either cordeau or primacord must be fired with a blasting cap, electric or properly fused, its business end fixed against a flat end of the cordeau by a small copper union. Under most circumstances the distance from a convenient point of firing to the charge is so great that the use of safety fuse alone would cause too much delay. Instantaneous fuse in combination with a length of safety fuse is an alternative to the use of electric blasting circuits, but has numerous applications of its own.

Firing multiple charges. Each charge must be properly set up, with a proper initiating device leading out. If electrical firing devices are used, the connector wires may then be joined so that the charges are electrically in series, and several series may be joined in parallel. In doing this care must be used not to exceed the voltage and amperage of the blasting machine, and the circuit must be tested in advance, using current so low that there is no danger of firing the charge. If primacord is used, a main line of primacord is run, and the cord from each charge is attached at right angles to the main line. One blasting cap on the main line will then fire all. Delay elements may be employed to space the firing of charges.

There are many methods of executing the exact details in practice, and each situation requires careful study and knowledge. Under some circumstances a series of charges close together can be fired by detonating only the first one, and the explosion will propagate by influence. This may be possible under water, or in moist earth where the charges are not too far apart.

Demolition. Explosives furnish a rapid and efficient method of effecting demolitions of all kinds for military and commercial purposes: railroads, track and equipment, roads, bridges, buildings and structures of all kinds, under-water obstacles in channels, or a submarine operating under water. The amount of charge may vary from a half pound to the several tons which, in several charges, may be necessary to destroy a sunken ship. By the use of relatively small charges of the more powerful explosives, blocks of solid metal and other compact masses which could not be touched by other methods, may be broken up. The proper placing of the charge is important to get desired results and economize on explosives. On land any of the explosives may be used, but the high explosives in general are of course the most effective, and difficult jobs in some cases can be done only with them. Under-water work obviously places some special requirements on the situation. All arrangements must be carefully waterproofed. Indeed, it is preferable to use explosives which are water-resistant, and for commercial work blasting gelatin is preferred. Wet conditions are often met on land. The explosion wave is especially powerful in water, and will crush barriers effectively at considerable distances from the charge. If, for example, an explosive charge is fired suspended in the water of a large water tank, the walls of the tank will be effectively destroyed.

Some Miscellaneous Explosive Effects. When a quantity of explosive is fired, it is immediately converted into a volume of gas which exerts a large pressure on its immediate surroundings. If the explosive is buried in ordinary earth, the pressure will produce a local cavity which may or may not extend to the surface, depending, as we have seen, on several conditions. A wave will further be propagated through the earth, radiating in all directions from the explosion center. Some of this energy will reach the surface in any case and be communicated to the air. The earth wave partakes of the nature of an earthquake wave, and can be detected at great distances by means of the seismograph. While the initial energy of the earth wave may be very large from a big charge, in ordinary earth the energy is lost very rapidly, and as little as 100 feet from a charge of several thousand pounds the earth wave will not be sufficiently strong to destroy the foundations of a well-built building. If the explosive is buried in a closely packed material, such as rock, there will be pulverization, shattering, and cracking in addition to the cavity effect, and the quality of this effect is related to the velocity of the explosion.

When the explosive detonates in the air just above the earth, a very powerful air wave is produced, which consists of a compression followed by a rarefaction. The earth receives some small part of the energy, as the air receives part of the earth-wave energy. The explosion wave in air is similar in some respects to a sound wave, registers itself as a noise, travels initially faster than a sound wave, but slows down until it ultimately becomes one. At a distance of 50 feet, the compression part of the wave from a charge of about 250 pounds of explosive covers a period of about .005 second and exerts a maximum pressure of about 6 pounds per square inch. The rarefaction is somewhat longer, about .020 second, and has a negative maximum pressure of about 2 pounds per square inch. This air wave is very powerful. At the explosion center, material objects will be fragmented into small pieces and moved outward with high velocities which may reach as high as twice the speed of a rifle bullet. At 50 feet, fragments may penetrate 1½ inches of mild steel. The fragments do not have good ballistic properties, and lose speed rapidly, but may travel more than ½ mile. Beyond the immediate explosion area extending only a few feet around the explosive, but within the 50-foot limit, the energy of the wave is sufficient to lift relatively heavy objects bodily and throw them considerable distances. People in this area may be killed by concussion, sometimes with no interior or exterior indication of physical injury. Damage to structures in the area is due largely to the slower action of the rarefaction part of the wave, and except relatively near the explosion center, walls, window glass, and the like, usually fall toward the explosion center. Windows may be broken up to 200 feet away.

A curious effect is sometimes noted where two powerful air explosion waves meet. The air may be so rapidly and highly compressed that it is heated to incandescence. Where the explosive is partially buried in the earth at explosion, as in the case of an aerial bomb which may detonate as soon as it strikes, after penetration of only a fraction of its length, or at varying depths, any combination of flame, fragmentation, blast effect, crater formation, and earth shock may be obtained. S. B. Smith[1] gives an interesting account of practical effects of bombs during aerial bombardments, but these matters must be considered in connection with the firing of any charge.

The effects of the explosion of very large quantities of explosive materials are interesting and useful as a guide in determining locations for explosive operations. At present newspapers have only too frequent accounts of such accidents. On September 21, 1921, what was probably the greatest man-made explosion in history took place—one which rivaled the natural explosion of Krakatoa. It occurred at the Oppau factory of the Badische Anilin und Soda Fabrik in Germany, and involved the accidental explosion in a storage house of an undetermined amount of ammonium nitrate which, however, was in the range of tens of millions of pounds. Nearly $50,000,000 of property was destroyed and 430 lives were lost in the explosion area. A crater was formed, which became a lake 250 feet in diameter and 50 feet deep. The air wave did damage in Frankfort, 53 miles away, and earth shock and sound reached Bayreuth, 145 miles away.

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[1] Smith, "Air Raids and Protective Construction," *J. Soc. Am. Mil. Eng.*, 33, 287 (1941). See also *Vibrations Caused by Blasting and Their Effect on Structures*, E. H. Rockwell, published by the Hercules Powder Co.

A famous explosion of the nineteenth century was at Stowmarket, in England, on August 11, 1871, where about 30,000 pounds of guncotton exploded in a powder magazine. All buildings to a distance of 200 feet were completely destroyed. In general, serious damage was confined to an area of 1,500 feet distance, although weak walls collapsed up to 4,000 feet. At 5 miles the air wave had force enough to bend an iron bar which was holding a door shut. Windows were reported broken up to a maximum distance of 7 miles, and the noise was heard at over 30 miles. In some recent engineering blasting operations, quantities of high explosive of this order have been fired at a single shot.

Hole Drilling. For many explosives operations, a hole must be drilled into the earth to receive the explosive charge. This drilling must be done with suitable equipment. If the amount of charge is small the hole may be of satisfactory diameter and size to receive the charge in the form of cartridges properly prepared, inserted, tamped and fired. There are many methods of loading holes, and the loading density of the explosive may be important. In practice this density is largely controlled by using cartridges of varying volume density of the different explosives, which are designated by the "cartridge count," that is to say, the number of cartridges in a 50-pound case. If the hole for any reason will not take cartridges, it may be necessary to fill it by pouring, using a granular explosive. If the amount of charge required is greater than the hole will hold or if it is desirable to have all the charge at the bottom of the hole, this may be done by "springing" the hole. This involves firing successively small *camouflet* charges in the hole to form and enlarge a cavity at the bottom. Care must be exercised to allow the hole to cool after each firing.

Coal Mining. This industry is one of the largest users of explosives, and employs black powder, high explosives in general, and the permissible varieties of explosives. The estimated use for 1940 was 274 pounds per thousand tons of coal produced, of which 115 pounds was permissible explosives, 106 pounds black powder, and 53 pounds high explosives other than permissibles, for a total coal production in excess of 500 million tons. Because of increased efficiency, the amount of explosives per ton of coal has been steadily decreasing, and the use of black powder, the only merit of which is its low-explosive effect that reduces pulverization, is falling even more rapidly in favor of special coal-mining high explosives which are also permissibles, such as some of the monobel dynamites. But black-powder pellet cartridges are extensively used at present.

Different types of mines, and each individual mine, present different problems, but in general the explosives are employed in horizontal drill holes, properly tamped or stemmed, and relatively small charges are used.

Other Mines and Quarries. Very large fields of application are also found in mines other than those for coal, and in quarries. For these, in general, pulverization of the product is not as important as in coal mines, and black powder is not as extensively used, although it is still employed where pulverization is a consideration. The use of permissible explosives is not as important a requirement, although fire-damp explosions must be sometimes thought of in any type of mine.

The explosives are also usually employed in drill holes but charges are relatively larger than coal blasts. These operations are highly specialized and require special study. With large charges in enclosed spaces the fumes generated by the explosion become of importance. In practice the fume characteristics of an explosive are often described as excellent, good, fair, and poor.

For an exact determination, the explosive is detonated in a Bichel gauge using a cartridge $1\frac{1}{4} \times 8$ inches or 200 grams of explosive, which is about equivalent. The volume of poisonous gas per unit weight of explosive is then determined chemically.

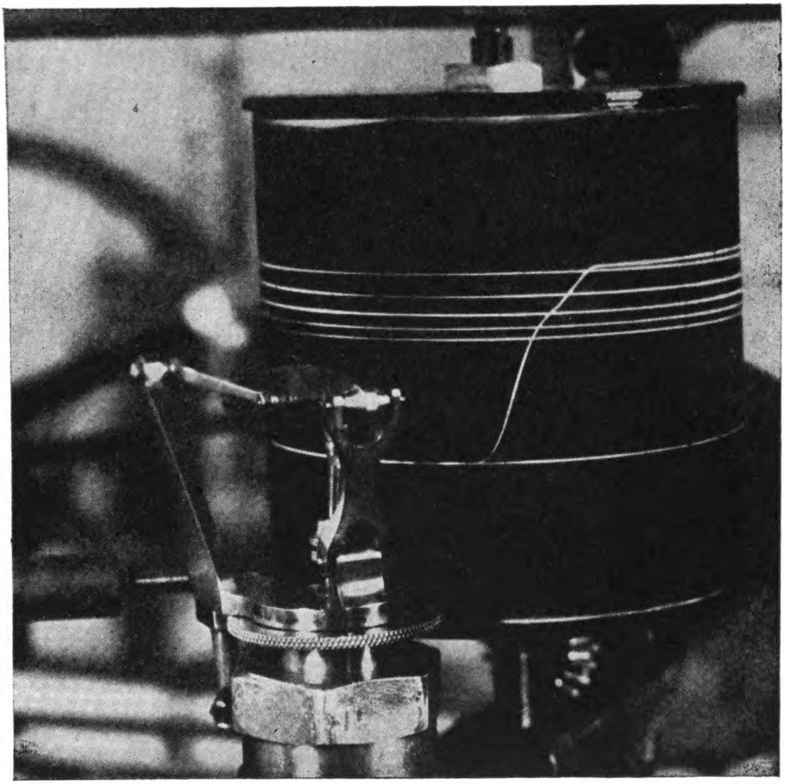
The United States Bureau of Mines classifies permissible dynamites for fumes in terms of their formation of poisonous gas per pound as:

Fume class A: <1.87 cu. ft.
Fume class B: 1.87–3.74 cu. ft.
Fume class C: 3.74–5.58 cu. ft.

The Institute of Makers of Explosives classifies dynamites other than permissibles on the same basis, as:

Fume class 1: <0.16 cu. ft.
Fume class 2: 0.16–0.33 cu. ft.
Fume class 3: 0.33–0.67 cu. ft.

The poisonous gases ordinarily to be expected in explosive fumes are carbon monoxide, oxides of nitrogen, and sulphur dioxide, but might include many others, such as hydrogen sulphide, cyanogen, and cyanides. The problem of explosive fumes is one of the specialized aspects of industrial toxicology, as well as the cause of casualties. Even when the proper explosive has been chosen for a difficult job, bad use may produce fumes in great excess of the expected amounts. For the reduction of fume formation, these considerations are impor-



Bichel Gauge

This apparatus records the amount of pressure generated at every instant during the split-second duration of an explosion. A study of the data obtained by the use of this apparatus aids in developing explosives to meet various field conditions and in making certain that explosives adhere to specifications.

(Courtesy of Hercules Powder Company)

tant: Use the largest cartridge diameter consistent with the work, avoiding diameters less than $1\frac{1}{8}$ inches. Do not use explosives deteriorated by any cause. Do not change the explosive wrapper or add other combustible material to the charge. Use a proper charge. Do not undercharge or overcharge. Where water is present have the charge properly prepared to withstand it, and fire as quickly as possible. Set up the charge carefully and properly so that misfires and burning do not occur. Always use proper tamping.

In some types of mineral mining the introduction of very small traces of chemical impurities from the explosive or fragments of the blasting cap may occasionally acquire importance.

General Construction Work. This may include building foundations and general excavation work, for bridges, roads, railroads, tunnels, shafts, pipe lines, well drilling, and a large variety of minor applications. These are specialized engineering operations. They require large quantities of explosives, thousands of pounds being frequently fired at a single blast. It therefore becomes imperative for reasons of cost of explosives and performance of the task at hand that the proper explosives be used and at their maximum efficiency.

This field is the one in which, apart from certain military applications, explosives receive the severest test of their ultimate possibilities of performance. They are used under all conceivable conditions in every geological situation. The largest individual charges are used here, also multiple charges; and thousands of cubic yards of material may be moved at one blast. The details of explosive application in any of the large engineering achievements at which the modern world wonders, are well worth investigating.

Agricultural Work. While not one of the quantitatively large uses of explosives, this field is one in which they find many useful applications, and various dynamites, nitramon, and related explosive mixtures are extensively employed.

Rocks and stumps (see Figure 73) may be removed by blasting out with a small charge placed at the base, which will also break them up to some extent. Rocks may be broken by placing an explosive charge, fused, on top, plastering it over with mud and firing. The explosive is placed where the rock would be hit if it were to be broken by a heavy sledge, and the practice is sometimes known as mudcapping and by other names.

Ditches may be built employing simultaneously a number of properly aligned buried charges which are essentially small crater charges (see Figure 74). The size and spacing of the charges are determined by such things as the nature of the ground and the width and depth of the ditch desired, but ditching cannot be done by this method in dry sand, thin muck, or gravel. The multiple charges can be fired in an electric circuit. In some soils which are just properly moist, only the first charge need be primed, and the detonation will propagate through the earth successively to the next charge at distances up to 3 feet, but this has to be tested out by experiment in each situation.

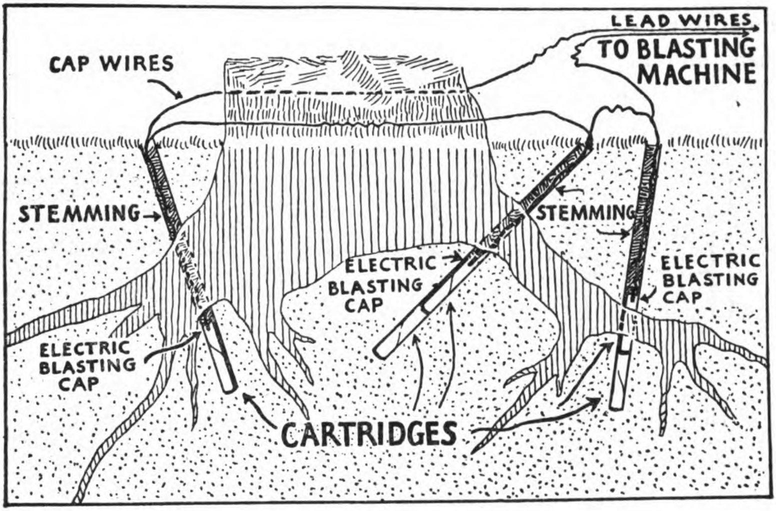


FIGURE 73: **Stump Blasting**

In large lateral-root stumps the charge is usually distributed as shown above.

(Courtesy of Hercules Powder Company)

In practice much of the earth under the usual conditions is blown into the air and scattered more or less evenly on the ground at the sides of the ditch, and this quantity may amount to 0.6 cubic yard per pound of explosive. It requires labor to place the charges in an extensive explosive ditching job but it has been said that one man with two helpers will open as much ditch in a day as 125 or 150 laborers with shovels, even with good shoveling, and the ditch will be a better one over-all. Using explosives the cost of a ditch 15 feet wide at the top, 5 feet wide at the bottom, and 6 feet deep may be $0.22 per foot.

Trees may be planted by lining up proper crater charges for the holes, and other agricultural uses include subsoiling, small dam construction, well construction, ice splitting, and log splitting.

Forestry. This field of use covers much the same ground as agricultural use, together with some aspects of construction, road building for example, and many specialized smaller tasks. The charges range from a fraction of a cartridge to several cartridges, as previously, and about the same explosives are used.

An interesting minor use of Cordeau-Bickford is in stripping bark from trees. Control of insect pests often requires that this be done. The cordeau is merely wrapped about the trunk of the tree and fired with a detonating cap. The bark is removed, much of the insect life is destroyed, and a tedious task is very rapidly and efficiently performed. The stripped bark is burned. Cordeau-Bickford may often be used alone where a small charge of explosive, less than the usual content of a cartridge, is desired.

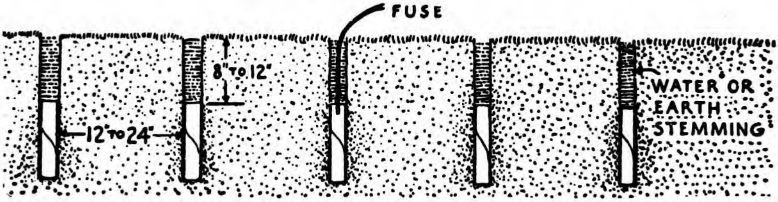


FIGURE 74: **Ditching**

Diagram of Cap and Fuse Method of Firing Propagated Blast

NOTE: If there is water in the hole, cap and fuse connection should be waterproofed.

(Courtesy of Hercules Powder Company)

Geophysical Prospecting or Seismic Exploration. An explosive fired in the ground sets up, it has been said, an earth wave which partakes of the usual nature of an earthquake wave. The waves may be detected by the seismograph, their characteristics may be measured and studied, and from the observations important information as to the constitution of the earth in the vicinity may be obtained. This field for the application of explosives is a relatively new but rapidly growing one. It places, however, a new series of requirements on explosives, especially in their practical forms.

Explosives for this purpose must be specially water resistant, very powerful to give waves which will be readily detectable over large areas within the limits of the instruments used, and have a high velocity of detonation. Blasting gelatin and gelatin dynamites are used for their power, but care must be employed to fire them under conditions of maximum velocity (see page 88).

For seismic prospecting it is necessary that the detonator not only fire the charge, but the exact instant of detonation of the charge must also be known. In using an electric blasting cap, there is some short lag between closing the electric circuit and detonation of the charge; in other methods, the delay is even greater.

This problem, known as that of the "time break," can be solved (1) by using an auxiliary electric circuit which will be broken by the charge—this will work with any method of firing; (2) by using electric firing and using the firing-line circuit as part of an auxiliary circuit; or (3) by studying the characteristics of carefully standardized electric blasting caps.

In the electric blasting cap the ignition mixture is fired by heat generated in a resistance shunted across the electric terminals. In the Hercules electric blasting cap this resistance is an 80% platinum, 20% iridium alloy, .00125 inch in diameter, and .11 inch long. The ignition mixture fires the detonator and in turn the main charge. At a current of 0.8 ampere the time lag is about .008 second. The bridge wire reaches higher temperatures and the time lag gets shorter at higher currents.

Knowing the time of closing of the circuit, the time lag may be taken from a time-lag-current graph if the current is known and the blasting caps are of sufficient uniformity. Hercules electric caps are said to have a time lag of .0047 second when fired singly at 1.5 amperes, with a maximum deviation of 17% and an average deviation of 6%.

Military Uses. Some of the military aspects of explosive use have been presented in detail. All members of the armed forces have some contact with explosives and explosive devices of the small-arms type, and with some of the smaller high explosive devices. The larger explosive devices are employed by specialized branches of all arms of the service, in both the Army and the Navy, such as the field artillery, coast artillery, chemical warfare, aviation, and the special subdivisions of the Navy. The task of learning their proper handling and use is a specialized course of instruction which is arduous though usually given rapidly.

In peace times, manufacturing of basic explosives materials in the United States is largely done in private plants, while much of the final loading and preparations of the actual charges is done at the government arsenals. In war times the volume of work expands enormously, and the overwhelming percentage is done in private plants, or at least not at the arsenals, large as some of them are.

Supervision of explosive materials between production and use is usually in the hands of ordnance officers, but on occasion may become the duty of any officer, and may, even in such cases, involve relatively large amounts of materials.

Some Miscellaneous Applications of Explosives. The enumeration of uses of explosives given covers the principal fields of large scale application with some illustrations in each case, but is by no means exhaustive. A few further examples will show this.

A recent, novel and specialized use now made in airplane construction is in riveting. In the usual process a rivet is set in place and then expanded to a tight fit and grip by a sharp blow which enlarges the end of the steel pin by compression. The same result may be accomplished by enclosing in a cavity in the rivet a small amount of an explosive charge which may be detonated by heat. Mild heating of the rivet fires the explosive charge and sets the rivet. Edmund von Herz in 1940 devised explosives for this purpose, and recommends,[2] as the base charge, lead azide mixed with 10–15% of tetrazine which lowers the otherwise fairly high ignition point of the azide (330°C.) to 145–150°C., but various mixtures may be used.

Some aircraft-engine starters are operated by explosives. A cartridge is put into a prepared seat to fire into one cylinder, "kick" the engine, and start it. Catapults for launching naval shipboard aircraft are driven by explosives because compressed air is too slow in action. The flame of a burning oil well may sometimes be "blown out" by a properly placed explosive charge. Explosives furnish a method of rapid demolition around the periphery of a spreading conflagration to confine it. Ice and log jams in streams may be broken by explosive charges. Fish may be killed and usually float to the surface as the result of the firing of an underwater explosive charge, but this is not a legitimate method of fishing.

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[2] German Patent (D.R.P.) 702,269, Jan. 7, 1941.

Similarly in the presentation of uses, the attempt has been made to preserve the balance of emphasis which is characteristic of a more normal world than the present. American armed forces, the Army and the Navy, seem shortly destined to exceed 11,000,000, and the number of military airplanes in use probably to exceed 100,000. No matter what figure one assumes as the probable use per unit, the arithmetic of the situation indicates that, with these forces in daily combat and airplanes employing four-ton "blockbusting" bombs, the total use of explosives will reach unprecedented levels, of which all the normal peacetime uses combined will be a fraction certainly less than 10% and more probably nearer 5% ultimately, and will be completely overshadowed by the outstanding military one.

Uses of Commercial Explosives. All commercial explosives are in the main chemically describable by the compositions which have now been enumerated. Most commercial manufacturers designate their explosives by names which are more likely to suggest the manufacturer than the composition of the explosive; until familiarity with them is gained, they can usually be identified by checking one's knowledge against the information in advertising literature.

The commercial explosives may be recapitulated from this standpoint:

Black powders. These are essentially gunpowders which may contain either sodium or potassium nitrate. The sodium nitrate powders are cheaper and are almost universally used for commercial blasting. They come in various degrees of fineness, as irregularly shaped grains, and also as pellet powders, a pellet being a cylinder about 2 inches in length, and from $1\frac{1}{8}$ to $2\frac{1}{2}$ inches in diameter, with a central hole about $\frac{3}{8}$ inch in diameter. Four of these pellets may be wrapped to give a stick similar in appearance to a dynamite stick. Low velocity of explosion and cheapness are its chief characteristics. It gives smoke and bad fumes.

Dynamites. Active-base dynamites are in general use in the United States. They come in stick, bulk, and free flowing forms; and are rated on the basis of their density, which is expressed by the cartridge count, and on their bulk and weight strength and nitroglycerine content. The strength is expressed as a percentage and may run from 15% to 100%. It does not express the nitroglycerine content because in an active base dynamite the other components contribute to the action. It usually refers to some specific performance test where the standard of 100% is the manufacturer's "straight" dynamite, in which the percentage rating does refer to the nitroglycerine content and 50% is the usual standard, although straight dynamites come up to 60%. For reasons given, the strength may not indicate performance in all work. Straight dynamite is water-resistant and powerful, but has bad fumes. Other dynamites have special characteristics for which the manufacturers' claims are usually reliable.

Ammonia dynamites. These contain ammonium nitrate replacing part of the nitroglycerine and range into special explosives like Nitramon, which is practically all ammonium nitrate. They are cheaper than other dynamites, with power enough for such uses as agriculture.

Gelatin dynamites. These have been described. They come in cartridges and plastic bulk packages. The percentage strength ranges from 20% to 100%, where 100% is blasting gelatin, and the percentage refers to nitroglycerine colloided nitrocellulose content. They are the strongest of all explosives and display the highest velocity but the dynamites have to be fired properly as they characteristically detonate at two velocities. They are water resistant but may have poor fumes although normally better than other dynamites.

Permissibles. These may be either special dynamites or gelatin dynamites with the addenda earlier described, as well as other explosive mixtures. The dynamites are usually of the Monobel or Duobel types and the gelatins are similar. Their rating is usually on the basis of cartridge count, velocity of explosion and class of fumes. Special low-velocity permissibles are made for coal-mining work.

All previous statements as to cost are relative, and actual costs vary with the time and place. At the present time 100 pounds of good-quality dynamite is worth in the neighborhood of $15. The explosive is one of modern man's most economical and useful tools. Wherever a tedious task has to be performed on a large scale, if any characteristic of an explosive is applicable, it will usually be found

TABLE 47

CHARACTERISTICS OF COMMERCIAL HIGH EXPLOSIVES

Types	Atlas Brand†	Weight strength	Number 1 ¼ x 8" ctgs. per 50-lb. case	Rate of detonation (feet per sec.) 1 ¼ x 8" ctgs. unconfined	Water resistance	Fumes	Consistency
Blasting gelatin	Blasting Gelatin*	100	100 to 110	20,000	Excellent	Fair	Rubbery
Oil-well explosive	Oil Well Explosive	80 to 100	Large Ctgs.	20,000	Excellent	Fair—Poor	Rubbery
Gelatin	Atlas Gelatin	20 to 100	85 to 110	6,500 to 20,000	Excellent	V. Good—Poor	Very Plastic
Ammonia gelatin	Giant Gelatin	30 to 90	85 to 110	7,000 to 20,000	Very Good	Excell.—Poor	Plastic
Semigelatin	Gelodyn*	65	107 to 126	10,000 to 11,000	Good	Very Good	Fairly Plastic
Nitroglycerine dynamite	Nitroglycerine Dyn.*	20 to 60	105 to 115	8,800 to 19,000	Fair	Good—Poor	Very Cohesive
Ammonia dynamite	Extra Dynamite*	15 to 60	105 to 115	7,300 to 12,000	Limited	Fair	Cohesive
Ammonia low density dynamite	Apcodyn	65	128 to 189	7,000 to 9,000	Limited	Fair	Cohesive
	Apex	20 to 70	Large Ctgs.	6,500 to 19,000	Lmtd.—V. Good	Poor	Granular
	Quarry Special*	65	133 to 170	8,000 to 10,000	Limited	Fair	Cohesive
	Quarry Special*	20 to 65	Bag Packed	4,000 to 5,500	Limited	Very Good	Granular
	Flo-dyn, Canyon Bag (1)	10 to 65	Bag Packed	4,000 to 5,500	Limited	Very Good	Granular
Gelatinous permissible	Gelcoalite*	35 to 55	97 to 126	8,200 to 16,400	Very Good	Good—Fair	Plastic
Permissible dynamite	Coalite, Apcol*	55 to 60	133 to 256	4,500 to 10,000	Limited	Fair	Cohesive
Seismograph dynamite	Petrogel No. 1 HV	60 to 100	Large Ctgs.	18,000	Excellent	Very Good	Very Plastic
	Petrogel	60	Large Ctgs.	16,000	Very Good	Fair	Plastic
Agriculture and logging dynamite	Farmex Ditching*	50	103 to 108	18,000	Good	Poor	Very Cohesive
	Farmex Stumping (2)	65	165 to 173	7,500	Limited	Fair	Cohesive
	Giant Stump. Powder (1)	15 to 65	105 to 162	7,400 to 9,000	Limited	Good—Poor	Cohesive
Low powder	R.R.P. and F. Powder (3)	5 to 20	100 to 110	4,000 to 9,500	Limited	Good—Poor	Granular to Cohesive

* Marked Giant in Western States.

† Dupont, Hercules, and others have both corresponding explosives and specialties. They are often designated by names such as Hercomite, Hercogel, for Hercules, or Agritol, Gelex, and the like for Du Pont.

(1) Sold only in Western States.

(2) Sold only in Eastern States.

(3) Marked Giant Judson Improved Powders in Western States. (Bag Packed)

The fume ratings given in this table are relative terms. The terms "good," "fair," etc., are used to furnish a basis of comparison of Atlas types and grades.

In this table each classification represents an entire series of explosives. For example, opposite the N. G. type explosives it will be seen that weight strengths are given from 20% to 60%, and velocities from 8,800 to 19,000 ft. per sec. This means that in the N. G. series there are available explosives that range from 20% to 60% in weight strength, and from 8,800 to 19,000 ft. per sec. in velocity.

(Courtesy of Atlas Powder Co.)

that, with any reasonable allowance for labor cost, the explosive will do it at least as efficiently, much more rapidly, and at a lower price.

Table 47 gives some of the recommended uses and characteristics of commercial explosives.

Discussion Questions and Exercises

1. Discuss the possibility of using colloided pyrocellulose as a coal-mining explosive.

2. Relate all of the operations and material required to produce a two-lined crater 10 feet in diameter in ordinary earth.

3. A 500-pound aerial bomb lands in the center of a 30-foot city street, and explodes on contact. Assuming the average circumstances, describe the results.

4. Report on the use of explosives in any large engineering operation.

5. Report on the names used by important explosives manufacturers to designate their commercial products, for example Atlas, Du Pont, Hercules, and the like.

6. Why are nitroglycerine explosives so largely used for general commercial work?

7. Can you think of any operation for which explosives are not ordinarily used, but might be?

8. Name some further uses of explosives which are not enumerated in the text.

9. If you were limited to one explosive substance for all possible uses, which one would most nearly meet all requirements?

10. Bring to class a newspaper account of any large-scale explosion, and discuss all aspects carefully.

11. Make the calculations of Chapter 6 for some of the commercial explosive mixtures.

CHAPTER 18

Packing, Shipping, Storage, and Safety

General Considerations. Explosives are potentially dangerous materials from the time the raw material enters the nitrator or the time when the first reaction takes place in which any nitrogen appears, under all circumstances, whether at rest or in motion, until the last pebble comes to rest after their final discharge. While practical explosives are chosen in part for safety, nevertheless for all circumstances safety is only a relative term in any case. Some operations are necessarily more hazardous than others. The most carefully investigated safety characteristic of an explosive is only, from the practical standpoint, a statistical statement implying a probability from which individual specimens may vary widely.

The immediate danger is to the operator and his close associates, but it extends to a surrounding area the extent of which increases largely as the quantities increase and concerns property and people who, as in many other situations in our civilized communities, go about their affairs calmly, sublimely and fortunately ignorant of the risks to which they are exposed. One of the limitations of the human mind, especially obvious in a book, is the inability to consider everything at once. Many of the dangerous operations have already been treated and this chapter will involve a certain amount of repetition, but at least it discusses operations in which the risk to outsiders is greater.

The law everywhere takes cognizance of all of these situations, and it is the first duty of a responsible individual to familiarize himself with and comply with the requirements, which in general are extensive and complicated although not nearly as much as in Europe. At present, in the United States (Chapter 1), no individual, the armed forces excepted, may legally possess explosives unless he has a federal license, and their transportation by any individuals on a public carrier is forbidden. Small-arms and ammunition are usually covered by local laws. Other situations and also the same ones are covered by regulations of other governing bodies, which may include the United States Bureau of Mines, the Interstate Commerce Commission, the state and municipal governments, and the local police and fire departments. Copies of pertinent regulations may usually be obtained by a proper application.

Law, however, is generally as inadequate a substitute for judgment as it is for self-control. Knowledge, experience, and common sense must be employed in every situation. Many of the safety recommendations in this chapter are those of the Institute of Makers of Explosives[1] whose pamphlet should be in the possession of all practical workers in the field.

Any quantity of explosive material greater than a few milligrams should be treated with consideration. After experience has been gained, surprisingly large quantities can be reasonably safely handled in experimental work,[2] but the very confidence which is inspired by experience is often the cause of accident, and one should not permit his own self-confidence to expose others. The story of accidents with fireworks is well known; their general use is fairly well regulated and has greatly diminished—almost to the vanishing point. The smallest commercial explosives device, the blasting cap, which contains as a rule not more than 1 gram of explosive, has been the cause of hundreds of serious injuries to children who get hold of them—and to experienced workers who allowed themselves to depart from procedures with which they were completely familiar. In these times, our newspapers bring almost daily accounts of explosions in explosives and munitions plants.

In all probability and contrary to a widespread belief, relatively few of these explosions are due to sabotage, although occasionally one may be. The explosives-manufacturing industry is an essentially hazardous one. Yet in normal times good practice and safety campaigns had reduced industrial accidents to surprisingly low levels which compared favorably with all other industries, and were better than those of many for which an outsider would ordinarily anticipate little risk. The rise in accident incidence is in all likelihood ascribable to the introduction of large numbers of inexperienced workers; many of them cannot, will not, or do not take the time to learn and obey instructions, which for individual operations are simple and straightforward, as a rule involve no mystery, and should inspire no fear. The total number of instructions for the entire field is large, but only one or a few are applicable to any specific operation.

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[1] *Safety in the Handling and Use of Explosives*, pamphlet #17, Institute of Makers of Explosives, 103 Park Avenue, New York, N. Y.

[2] An important teaching problem is to overcome the unreasoning fear which most people, even otherwise intelligent and educated ones, including chemists, have for explosives, without creating an attitude of carelessness or even bravado. One should not have fear, but he should employ unremitting caution.

Packing. United States Army specifications prescribe packing and containers for the bulk explosives and some of these have already been described, for example gunpowder and the initiators.

Pyrocellulose is usually not packed for general use, except in compressed charges in explosive devices, as depth bombs. As smokeless powder, it may be packed in a variety of ways, the first of which is as the charge in fixed ammunition which may be anything from a .22 cartridge to the 6-inch gun ammunition, weighing up to 150 pounds. Fixed ammunition is usually packed, so many rounds depending on size, in cardboard or fiber containers, which may in turn be packed in wooden boxes (page 384). For the larger sizes there may be only two or four rounds per box. Since one end of the ammunition is heavier than the other there is usually alternation to bring about even distribution of weight. The boxes may be end opening and provided with a seal which must be broken to open the box. A card containing detailed information about the ammunition is enclosed, and the box itself is stenciled with a variety of information.

Made-up single separate-loading charges may be packed, with or without igniter pads pinned to them, in sealed cylindrical metallic containers. For bulk powder the standard container is a zinc-lined wooden box or steel container about 26 × 16 × 11 inches; there are several types, two of which have capacities of 110 and 140 pounds. The cover of the box is arranged with locking rings and a rubber gasket and a lever on top of the box works on a lug to give an air seal. Boxes are tested before filling by drilling a small hole in the cover, and using a gauge and compressed air, and must hold an air pressure of 3 pounds for 1 minute, as well as withstand a water submergence test. In storage, boxes are usually piled six high on their narrow sides at an angle of about 20°, to permit insertion of methyl violet test paper.

T.N.T. and amatol in blocks or bulk are packed in wooden containers. Ammonium picrate and picric acid must not be in contact with metal because of the danger of forming metallic picrates which are much more sensitive; hence both are usually packed in wood. Dynamite, gelatins, and other commercial explosives in the form of cartridges are packed in fiber or wooden containers, so many cartridges to the container weighing 35, 50, or 100 pounds. Bulk packages in nonporous bags may be similarly packed. Ammonium nitrate can be packed in bulk in any convenient form, but is very soluble in water.

Fulminate and lead azide in bulk are packed wet with not less than 20% of water, or with not less than 33% by weight denatured alcohol in heavy cotton twill cloth or duck, with a top cap of the same material. The bag is tied and enclosed in a strong grain bag which is tied and placed in a barrel, in which it is surrounded by not less than 6 inches of sawdust. The barrel is lined with a heavy jute bag securely closed to prevent escape of the sawdust. After cooperage, the barrel is filled with water and the bung is sealed. It must be tested for leakage and should not contain more than 150 pounds of dry weight of the initiator. In general initiators require the maximum of care, and are not dried out till used.

Blasting caps and military primers and igniters are usually packed in sealed metallic containers, so many per package depending on size. Cordeau-Bickford and Primacord come on reels with outside wrapping and have been described. Fireworks devices are usually packed in wooden containers, and are often embedded in sawdust or other materials.

Bombs, shells, and other explosive devices may be crated in wood. When packed in railroad cars they may be put in standing directly on a flat end, bombs with vanes removed, and all unfuzed. They are packed carefully but tightly in rows with heavy criss-cross wooden separators to prevent motion and contact; in the case of shells care must be exercised to avoid injury to the driving band, which is given separate wrapping. All packing is usually appropriately marked externally and contains additional information internally.

In the laboratory, where as a rule very small amounts of explosives are employed, glass bottles (preferably with cork or rubber stoppers) should be used; but where amounts are larger than a few ounces, the same rules which govern elsewhere in corresponding situations should maintain. In any event, the main supply should be accessible only to one responsible person, students should possess at any time as little as possible. Pyrocellulose and initiators in any quantity should always be kept wet, and dried before use. Nitroglycerine should not be kept at all, but should be destroyed immediately after use. If it must be kept, it should be mixed with at least an equal volume of methyl alcohol from which it can be extracted by dilution with a large quantity of water.

Unpacking. Opening packed explosives must always be done to some extent with tools which are appropriate to the job. Wherever possible, metallic tools should be avoided, particularly metal hammers and wedges, for which hardwood wedges and mallets should always be substituted. This precaution is particularly important in the case of pyrocellulose, gunpowder, and initiating explosives. Blows should be avoided in favor of pressure. In opening lock-cornered wooden cases it is safer to split the box by starting a crack at a corner about 1½ inches below the top with one blow of a wooden mallet and wedge, doing the same at the other corner, and then carrying the split around the box to remove the top completely, rather than to try to pry the top of the box off.

Where metal must be used, copper and lead are safer than the harder metals like steel. Instructions usually give directions for unpacking specific containers and should be carefully obeyed.

Transportation. Law covers all phases of transportation on common carriers, and to some extent in private shipment by truck and other vehicles. The vehicle must usually be properly marked with the word "Explosives" or carry a red flag with the word "Danger" in white letters of prescribed size. It should be in good condition with a tight wooden floor, and metallic contact with the explosive must be prevented. Fire extinguishers must be provided, smoking prohibited, the electrical system and other devices likely to cause sparks or excessive heat given special attention, and inspection and other details are usually legally covered. In travel, congested areas must be avoided and shock and jolting minimized.

Initiating explosives and devices should never be carried together with other explosives; in fact, in all circumstances these should be kept as far apart as possible up to the actual point of use. Certain combinations of explosives should be avoided, and if possible it is well to handle only one kind at a time.

Cases received in damaged condition require special attention. The case may be repaired with wooden tools, or if repair is not possible it may be placed as a whole in another wooden box surrounded by sawdust, clean cotton waste, or wadding of newspaper. Any loose explosive should be swept up and burned, along with broken parts of cases. Packing cases, or wrappers of any kin d. which have been used for explosive materials should never be used for any other purpose, but collected and burned as regularly as possible.

Storage. The storage of explosive materials is related to various other aspects, including manufacturing, and transportation, and may be more or less permanent. Proper storage is a question not only of safety but to a very considerable extent of economy. Temporary storage should conform as nearly as circumstances permit to the best practice, which under some circumstances cannot be very closely. The main guiding principles are: location, construction, size; nature of materials to be stored; ventilation and control of temperature and humidity, with the related considerations of protection from weather; impact of bullets and projectiles, fire, shock; any other environmental hazards; the establishment of routines for those having access; and survey.

Location. Storage places for explosives, known as magazines, arsenals, and the like, are usually located where an accidental explosion will cause a minimum of harm. Laws and common sense prohibit permanent storage in any densely populated area, and local authorities usually frown upon even temporary storage of relatively small quantities. Isolated ravines form natural barricades, and a hill gives a barricade on one side. In the case of a manufacturing plant the differences in level may be utilized for the transport of materials by gravity. Earth barricades, wide at the base and narrowing to the top of the height of the buildings, are usual both for plants and storage. Entry tunnels are zigzagged like military trenches to prevent enfilading in the case of an explosion.

Distances—from inhabited buildings, public highways, railways, other magazines, and buildings—are important and some are prescribed by the American Table of Distances. Blasting caps and other detonator devices should always be stored alone and never less than 100 feet away from any other magazine. Fewer than 1,000 blasting caps or less than 50 pounds of explosives do not require a separate building; more than 20 million blasting caps or 500,000 pounds of explosives may not be stored in one building. Table 48 gives some requirements, assuming the use of barricaded buildings—otherwise the distance must be doubled; the quantities are maximal. The magazine distances are military, but military requirements for the others are more than twice as great.

TABLE 48

DISTANCE REQUIREMENTS FOR STORAGE OF EXPLOSIVES IN BARRICADED BUILDINGS

Blasting caps, total number	Explosive, pounds	Other magazine, feet	Inhabited building, feet	Railway, feet	Highway, feet
25,000	50	60	73	45	23
50,000	100	80	120	70	35
500,000	1,000	180	510	305	155
1,000,000	2,000	200	600	360	180
12,500,000	25,000	300	1,055	635	315
	100,000	400	1,815	1,090	545
	500,000		2,705	1,620	810

Magazine Construction. The foundation for the magazine may be brick, concrete, or stone. The walls above the foundation may be of soft brick laid in a cement mortar containing not over 25% lime. Construction is designed to avoid large, hard fragments in the event of explosion. The walls may also be of double wood sheathing, or hollow tile, but the hollow wall should be filled with dry, well-tamped sand to protect against bullets, up to 14 inches being required for service ammunition. The walls may be built of galvanized iron, or the outer wall may be fire-protected with No. 26 gauge galvanized iron secured with galvanized nails and lead washers.

The roof should be wood frame and sheathing, covered with galvanized iron or tin, and bullet-proofed with sand. All outside woodwork should be fire-protected with galvanized iron. Doors should be built of solid bullet- and fireproof construction. Floors should be wood.

Ventilation should be provided at the floor and ceiling level. A false roof creating an air space, shade, aluminum paint, and all other devices to protect against excessive temperature changes are worth consideration. A maximum and minimum thermometer and record should be part of the routine, and excessive dampness should be avoided.

A temporary magazine may be of frame or tent construction, or an excavation in a hillside if the earth is dry. Explosives kept necessarily in the open should be off the ground, protected at least by a tarpaulin. Curiously enough, it is said that animals will eat some of the bulk explosives.

Storage of Explosives. Black powder is very sensitive to sparks and to deterioration by moisture. It should preferably be stored alone and not with picric acid, dynamite, or other high explosive. Smokeless powder should likewise be stored alone, and temperature changes are of importance; it may be stored with black powder if necessary.

T.N.T. is usually stored in a standard magazine approximately 26 × 42 feet in size, of about the construction described, and while this magazine was originally designed for 250,000 pounds, usually as a matter of convenience it contains 100,000. In a magazine area such magazines are spaced at distances of 400 or 800 feet. T.N.T. will usually burn quietly, but after a large amount begins to burn no attempt should be made to fight the fire as it will ultimately detonate almost certainly. Picric acid and ammonium picrate have about the same requirements as T.N.T. The dust from picric acid is a hazard, as it is difficult to hold down, and can cause explosion. Ammonium picrate readily absorbs moisture, and this reduces its strength and sensitivity. Picric acid is better stored alone.

Tetryl is one of the more sensitive high explosives; it should be stored alone. It is regarded as partaking of the nature of the initiating explosives, which in bulk or in the form of primer devices are never stored with anything else.

All of the ammonium nitrate explosives, including amatol, deteriorate very rapidly with dampness. Dynamites and all nitroglycerine explosives are sensitive to temperature change and liable to freezing unless they are of nonfreezing types. After freezing, dynamite must be thawed. Thawing will occur of itself on long standing at a higher temperature, but can be done using hot water in a double boiler, the dynamite being in the dry inner kettle. Under no circumstances must a flame be used in connection with the thawing kettle, in which only hot water is to be used. Thawing of dynamite has in the past been a large source of accident.

Ammunition can be stored in packing cases in magazines. Bombs (with vanes removed) and shells may be stored standing on their bases, with space between, and also piled in pyramidal heaps lying on their sides.

In general, in large permanent magazines, complete separation of different types of explosives can be secured. Failing this, high explosives and low explosives must be kept apart and initiators must be kept away from both. Combining of quantities of a sensitive explosive with larger quantities of a less sensitive one must be avoided, anywhere. In a well-built magazine, temperature and moisture control are provided for, as well as protection against fire hazard; under exceptional conditions all these must be thought of and provided for as well as circumstances permit. The small quantities of explosives required in general everyday use are conveniently stored in heavy, specially built wooden boxes provided with lock and key.

Magazine Operation. In military practice, magazines are most carefully operated; so also are the larger private magazines, and so also should be any storage place—large or small. The important considerations are: maintenance of conditions which will give the explosives materials the maximum length of life; avoidance of fire risks inside and out; elimination of unnecessary disturbance of any kind, with special reference to the eccentricities of the materials stored; and the use of routines to circumvent human frailty in the necessary handling which must occur.

Atmospheric conditions which are good for humans are good for explosives—good ventilation, average humidity of about 70% (too dry is bad as well as too wet), and a moderate even temperature of about 70°F. Higher temperatures are very undesirable, and for smokeless powder in particular the temperature should never go above 80°F. for more than 3 days. A lower temperature is not as harmful, but with too low temperatures there is danger of dynamites freezing, and excessive variations will deteriorate explosives even when the extremes are not in themselves too bad if maintained as steady temperatures. Conditions should be checked by recording instruments.

Careful attention should be paid to the characteristics of explosives with regard to storing them together, and in general when the total amount is in excess of 1,000 pounds they should be stored alone. In any event, different explosives should be as widely separated as circumstances permit. The containers should be kept off the floor by skids to permit circulation of air beneath a pile.

One person should be in responsible charge and the duty should be a direct personal one. In a small storage place he should be the only one who has access. A copy of the regulations for conduct, thoughtfully prepared with respect to the situation then maintaining as well as with usual safety precautions, should be conspicuously posted within.

Repairs of cases and other mechanical work should not be done in the storage place, and loose explosives in general should not be removed from storage containers within the building. All cases should be cleaned of all foreign material before storage, and the interior should be kept clean. Empty cases should be promptly removed, and burned regularly.

No smoking should ever be permitted, and no matches should be brought into the storage place. Electric connections, and occasional unusual sources of static charge, sparks, or heat should be considered. Rubber-soled or safety shoes should be worn, and metallic objects on the person avoided. Only safety tools—wood, copper, lead—should be brought into the storage place. Necessary handling should be as gentle as possible, not by rolling, sliding or dropping. Any loose explosive which does get out of containers should be immediately picked up, taken elsewhere and destroyed. Deteriorated explosives should be promptly removed and destroyed. Explosives should be stored so that older material is used first. It will be if it is first reached.

For complete cleaning a storage house should be emptied first. Spilled nitroglycerine or stains are removed with rubbing with a stiff broom, mop, or brush after flooding the house with a solution (by volume) of 1.5 parts water, 3.5 parts denatured alcohol, 1 part acetone, and $\frac{2}{3}$ lb. of commercial sodium sulphide (60%) per gallon. The area outside of a storage place should be kept free of rubbish and combustible material, and grass, leaves, and brush should be cut and removed and not allowed to accumulate. Government regulations and instructions of the manufacturer[3] should be consulted and followed in appropriate situations.

Survey of the storage place involves largely checking on the satisfactory fulfillment of the precautions summarized above. Deterioration of smokeless powder is indicated by the test strip of methyl violet paper which may turn salmon pink, and is replaced every 6 months or a year. A smokeless-powder magazine will normally smell of ether, but an excessive smell indicates a defective storage case. Chemical tests are not usually performed on explosives in storage, but they may be; and deterioration is determined by visual examination. For dynamite explosives, hardness, discoloration, excessive softness, or leakiness shown by the oily stains of nitroglycerine on packages, indicates deterioration.

Deteriorated explosives are always destroyed. This may be done by exploding them in a safe place. It may also be done by burning, in small amounts at a time. This must always be done carefully and requires specific instructions for each explosive if the amount is in excess of 10 pounds. Destruction by burning should always be conducted on the assumption that detonation will occur. Blasting caps are usually destroyed by detonating not more than 100 at a time, using a hole in the ground and a dynamite primer of about half a stick.

Hazardous Situations. Some hazardous circumstances which arise are listed here, with a few of the appropriate precautions.

Transportation of explosives from the storage place to the point of use. The important precautions are careful handling, avoidance of water, flame, fire, or sparks from electric current, and keeping of detonators separate. One person should carry the detonators only.

Disposition of explosives at the point of use. A great many factors enter into this, and it may involve what amounts to secondary storage centers.

Necessary mechanical operations such as opening cases. See the discussion on page 411.

Fusing blasting caps. A procedure has been given for this (page 332). In practice it is a prolific source of accident, and a list of do's and don't's, of which many are available, should be studied carefully.

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[3] Ordnance Technical Regulations, Ordnance Safety Manual O.O. Form No. 7224, and manufacturer pamphlets.

Attaching detonator to the primed cartridge. The comment immediately preceding is appropriate to this situation (also see page 390).

Loading and tamping charges. The possibilities of these operations involve not only the danger of firing the charge by careless or improper procedure, but also inefficiency of firing or failure to fire, which may have later elements of danger. Unexploded charges, known as misfires, may be dangerous in subsequent work.

Firing shots. The charge must not be fired until the ground is clear of those likely to be injured by the blast. This precaution involves adequate warning. When using electric firing this is not difficult; but when using fuse firing, the time of delay must be long enough to allow the operator to escape, and hazards may arise during the period in which little can be done.

Returning after the blast. Sufficient time must be allowed for all missiles to come to rest.

Misfires. Misfires of high explosives are dangerous because they leave material which may later be exploded accidentally by the mechanical operations which must be performed at the site. A workman may hit an unexploded charge with a pick or shovel, with consequent injury or death. Misfires may be reduced very largely by proper storage of material to prevent deterioration and by proper preparation of all the elements of the firing operation, and minimized by proper checking of results. Interest is attached nevertheless to the attack on this problem from the angle of the explosive itself.

If a piece of ordinary cotton is dipped in liquid air and then put in a flame (this may be performed as an experiment), it deflagrates. While the liquid air remains absorbed the mixture is a high explosive and can be detonated by any initiating detonator like any other explosive. After 30 minutes or more the liquid air evaporates completely, and the cotton returns to its original harmless condition. Liquid air may thus be absorbed in powdered charcoal, coal dust and other things.

These are essentially mixture explosives but using carbon the essential reactions are:

$$C + \tfrac{1}{2}O_2 \rightleftharpoons CO + 26{,}428 \text{ calories},$$

or

$$C + O_2 \rightleftharpoons CO_2 + 94{,}385 \text{ calories}.$$

Other products are formed from other materials. It is impossible in practice to get complete conversion into carbon dioxide but the total energy involved is still very large, the velocity of detonation is high, and the action compares favorably with the most powerful high explosives.

Because they almost eliminate the possibility of misfires, such explosives have received much attention, and have also been proposed for military purposes. Other liquid gases, such as carbon dioxide in combination with electric and chemical heating elements, have been similarly considered.

Practical Bugs. Some of the more ordinary sources of difficulty in the operation of explosive devices, with their method of cure, are listed.

Failures with miners' squibs:

CAUSES	MEANS OF PREVENTION
The squib may have been damp.	Keep squibs dry. Do not leave them lying around the mine loose or in an uncovered box.
A little water in the hole through the tamping may have extinguished the squib before it reached the primer.	In damp holes use a blasting barrel and shoot a squib through it to clear and dry it before putting it into the hole, or, better still, use electric squibs or fuse.
A small piece of stemming may have dropped into the hole for the squib and clogged it.	Use damp clay stemming and pack it tight. Be sure the miner's needle is smooth and straight and remove it very carefully.
With stemming material wrapped in paper, the paper may have buckled in tamping and been dragged into the hole by the removal of the needle.	Do not use paper-covered dummies for tamping around a miner's needle. Use loose clay.
The squib may have been thrust too far into the hole.	Leave a little of the body of the squib containing the powder extending from the hole.
With pellet powder, the miner's needle may have been thrust between the side of the pellets and the paper shell or between the shell and the wall of the bore hole instead of into the central perforation of the pellets.	Be sure the point of the needle is in the central perforation of the last pellet. Do not crush any of the pellets.

Failures with safety fuse or with blasting cap and fuse:

CAUSES	MEANS OF PREVENTION
Wrong grade of fuse may have been used.	Use waterproof fuse in wet work and suitable fuse in other work.
Fuse may have become damp in improper storage.	Store fuse in a cool, dry, well-ventilated place.
Fuse may have been kept so warm as to cause the waterproofing material to melt and strike into the powder train, or to cause the fuse to dry out and crack so that water penetrated to the powder.	Store fuse in a cool place. Do not leave it near stoves, radiators, or steam pipes.
Fuse may have been cracked by uncoiling it while cold and water may have penetrated to the powder.	Warm cold fuse at a temperature of from 70° to 80°F. for eight hours before uncoiling it.
Fuse may have come in contact with oil, such as gasoline or kerosene; or grease may have been used for waterproofing, from which oil may have penetrated to the powder.	Keep fuse away from any oils in transportation and storage. Do not use grease for waterproofing. Most greases contain light oils. Do not use paint as a waterproofing material if it contains a light oil drier. Use a cap-sealing compound, miner's soap, or wax.
In a wet hole water may have been forced through the waterproofing of the fuse into the powder train by excessive pressure in tamping.	In holes full of water, especially in shafts, use waterproof fuse with cap sealing compound and tamp carefully to prevent the development of too much pressure.
Fuse may have been injured by coarse, sharp stemming material or by a metal tamping bar or by rough or careless tamping.	Use fine stemming material, preferably sand or clay, free from all sharp particles. Use wooden tamping bars and tamp carefully, but firmly.
Protective coverings of fuse may have been broken by making sharp bends or kinks in the fuse, thus allowing moisture to damage the powder core.	Do not make sharp bends or kinks in fuse, especially in cold weather.
Use of short fuse and consequent hasty loading and tamping may have resulted in rupturing the fuse covering and allowing moisture to enter the powder train.	Cut fuse long enough to extend out of bore hole and load and tamp carefully.

CAUSES	MEANS OF PREVENTION
With pellet powder, the fuse may have been pulled out of the primer cartridge in loading and tamping.	Run the fuse all the way through the primer cartridge, double the end back into the hole, and pull the fuse tight. Do not tie a knot in the end of the fuse.
With pellet powder, the fuse may not have been gashed or cut properly at the end.	Gash the portion of the fuse that will lie inside the primer cartridge three or four times, cut the end on a long slant, and turn this end back into the central hole of the cartridge in such a way as to open the gashes and bring the powder train in the slanting end against the wall of the pellet, not against the fuse.
End of fuse may have absorbed moisture from the atmosphere so that it did not burn through to the explosive in the cap.	Unless fuse is freshly cut from the roll for each cap, cut ½ inch off the end just before inserting it in the cap.
In cutting the fuse, its waterproofing material may have been smeared over the end of the powder train so that this melted on the explosive in the cap and prevented it from igniting.	Be sure that the knife blade, or the cutting device of the cap crimper used for cutting fuse, is clean and sharp. Do not cut fuse with an axe, spike, file, pliers, or any dull or blunt edge.
Fuse may have been cut at such a slant that on being inserted into the cap, the end became doubled back and prevented the spit of the fuse from striking the explosive in the cap.	Cut fuse straight across with a clean sharp knife or fuse cutter.
Fuse may not have been pushed all the way down to the explosive in the cap.	Always be sure that the end of the fuse is seated squarely on the explosive in the cap. If the end of the fuse is too large to enter the cap easily, cut off a small piece with special care not to spread the fuse and try again. If this fails, hold the end of the fuse straight upward and roll it slightly with the finger and thumb or reshape it with the crimping jaws of a sleeve-type cap crimper, taking care that the powder does not fall out of the fuse.

CAUSES	MEANS OF PREVENTION
The powder may have dropped out of the end of the fuse and the spit may have been smothered by the wrapping before it reached the explosive in the cap.	Never whip the ends of fuse or handle them in any way so that the powder may fall out.
Fuse may have been pulled out of the cap in loading the primer and tamping.	Never attempt to crimp the cap on the fuse with the teeth or a knife. Use only a cap crimper of approved type and make a tight crimp.
Fuse may not have been lighted.	Be sure that each fuse is really burning before lighting the next. Use lead spitter, hot-wire lighter, or other sure means of ignition in wet work.
Blasting cap may have become wet or damp in storage. It is possible for humidity alone without actual precipitation to make the explosive in a cap too damp to explode.	Store blasting caps in a dry, well-ventilated place.
Water may have dropped into the cap, or humid mine air may have condensed in it.	Always replace the felt pad and lid on the cap box immediately after removing a cap and keep the box in a place protected from rain or dripping water. Do not leave caps in the mine overnight.
Moisture may have been introduced into the cap by blowing in it to remove foreign material.	Never blow into a cap.
Some such foreign material as sawdust may have gotten into the cap and formed an obstruction between the spit of the fuse and the explosive.	If foreign material is suspected in a cap, tap the open end lightly on dry wood, or on the thumbnail.
Oil may have gotten into the cap. Even highly inflammable oil will reduce the strength of a cap and may drown the spit of the fuse.	Do not use any grease or paint containing light oil to waterproof the joint between cap and fuse, for the light oil will work its way down through the slightest crack into the cap. Use waterproofing compounds manufactured for this purpose.

CAUSES	MEANS OF PREVENTION
Water from a wet bore hole may have penetrated into the cap.	Crimp the cap on the fuse tightly and dip the joint in cap-sealing compound a few hours before making the primer. If a smooth covered fuse is in use, a watertight joint can usually be made with a cap crimper which leaves no vent and no waterproofing will be needed.
The cap may have been pulled out of the primer in loading and tamping.	Tie the fuse securely to the primer cartridge and load carefully.
Fuse may have been laced through the primer cartridge.	Never lace fuse through dynamite. Make primers by approved methods.
Primer cartridge may have been cut off by adjacent shots.	Place primer near the bottom of the hole. If the fuse has burned beyond the point where the collar is blown off, it will probably keep on burning and fire the cap.
Holes may have been cut out of the round by making fuses too short to give proper rotation or by lighting them in wrong order.	Be sure to have fuses long enough to give proper rotation and to light them in correct order.

Failures with electric blasting caps and delay electric blasting caps:

CAUSES	MEANS OF PREVENTION
Electric detonators may have been damaged in improper storage. Dampness is likely to affect the cap or corrode the wires so that they break easily.	Store electric detonators in a dry, well-ventilated place.
The bridge wire of the cap may have been broken by jerking the wires or other rough handling.	Handle electric firing devices carefully. Test each cap with a circuit tester before making the primer and before connecting the wires in the blasting circuit.
The cap may have been pulled out of the primer in loading and tamping.	See that the cap is securely tied or otherwise fastened in the cartridge, and load carefully.
There may have been a break in the blasting circuit.	Test the blasting circuit with a circuit tester before attempting to fire.

CAUSES	MEANS OF PREVENTION
In scraping insulation from No. 18 or finer wire with a knife, the wire may have been so nearly cut in two that it separated after connections were made, causing a break in the circuit difficult to find.	Uncoil the layers of insulation from this fine wire instead of scraping them off with a knife.
Poor connections may have created such high resistance in the circuit that the current was not strong enough to fire all the detonators.	Scrape or sandpaper the wire ends until they are clean and bright and twist them together tightly. Do not make loop connections.
A wire of waterproof electric blasting cap may have been cut and the connection made without scraping off the enamel under the cotton insulation.	Do not cut wires of waterproof electric blasting caps. Make connections on the tinned ends. If absolutely necessary to shorten wires, make sure the enamel is thoroughly scraped off.
A piece of wire cut from a waterproof electric blasting cap may have been used for connecting wire without scraping off the enamel.	Do not use leg wires of caps for connecting wires. Use only regular connecting wire.
The blasting machine may not have delivered a current of sufficient amperage and voltage to fire all the caps.	Make sure that the blasting machine is of sufficient capacity and in good condition. Test it with a rheostat.
The blasting machine may have been wet so that a short circuit was set up in its mechanism.	Keep blasting machines dry. Do not leave them underground overnight.
The blasting machine may not have been operated hard enough to develop its full capacity.	Always operate a blasting machine with all possible force. Operate the machine two or three times to magnetize the field magnets before connecting the leading wires.
Parallel or multiple connections may have been made for firing with a blasting machine. Blasting machines are not designed to develop sufficient current for ordinary parallel or multiple connections.	Always connect all the caps in one series for firing with a blasting machine or, if circumstances require it, in a graded parallel series.
The power circuit may not have delivered a current of sufficient amperage and voltage to fire all the caps. A generator of sufficient ca-	Be sure that the power line is actually delivering adequate current at the time and place the blast is made. Do not attempt to fire a

CAUSES	MEANS OF PREVENTION
pacity may be running at full speed, but unless it is actually delivering the power at the instant of firing, the interval of time necessary to build up the current is likely to cause trouble.	series circuit with an alternating current of fewer than 40 cycles.
Leading wires of too small gauge and consequent high resistance may have been used, thus reducing the current delivered to the caps.	Use nothing smaller than No. 14 leading wire for a circuit containing more than three caps.
The wires may have been half-hitched around the cartridge and the insulation may have worn through, causing a short circuit.	Make primers so that wires do not cross each other.
The insulation of the wires may have been rubbed off by too forceful tamping with a metal bar, causing a short circuit, or a wire may have been broken in this way.	Use wooden tamping bars and tamp carefully.
Worn insulation on leading wires or an untaped splice or wet leading wires may have caused a short circuit in these wires and leakage from the blasting circuit. Short circuits are especially likely to occur in duplex leading wire under these conditions.	Do not use duplex leading wire where more than one cap is to be fired in one shot. Use well-insulated single wire, rubber covered for wet work. See that leading wire is dry and in good condition. Test it for short circuits with a circuit tester.
Leading wires or connecting wires may have come in contact with rails, pipes or machinery and caused a ground or short circuit.	Keep all wires of a blasting circuit out of contact with any metal object.
Joints in the wires may have lain in water or on wet ground and caused a short circuit.	Tape wire joints carefully or keep them away from contact with water or wet ground.
In wet work, or only slightly damp work where the rock or earth contains mineral salts, there may have been enough leakage of current from the circuit to cause the caps in the middle of a series to misfire.	Use electric blasting caps with enameled wire or parallel connections; in sea water or other hard water use both.
Too many electric blasting caps may have been connected in one	Never connect more than 50 ordinary electric blasting caps in

CAUSES	MEANS OF PREVENTION
series, resulting in current leakage from center caps.	one series even in dry work; in wet or damp work, and if the water is hard, use blasting caps with enameled wires.
The wrong wires may have been connected with each other.	Be sure that all wires are connected so as to give a continuous path for the current without cutting any of the caps out of the circuit.
Two different makes of detonators may have been used in the same series or multiple series. Electric blasting caps of different manufacturers have different firing characteristics.	Be sure that all detonators in any blast are of the same make.
The collar of the hole and the primer may have been cut out of the round by the explosion of an adjacent hole.	When firing rotation shots place the primer near the bottom of the hole.
Holes may have been cut out of a round by placing the wrong delay in the wrong hole.	Observe the tag numbers carefully and place the right number in the right hole.

Failures with delay electric igniters:

CAUSES	MEANS OF PREVENTION
The causes listed for failures with electric detonators apply also to delay electric igniters.	Follow the same precautions.
Many of the causes for failures with fuse and blasting caps apply also to delay electric igniters.	Use the same precautions in handling this fuse as with ordinary fuse and especially in attaching a cap to it. Be sure to cut off at least $\frac{1}{2}$ inch of the igniter fuse before attaching a cap.
The rubber sheath of the igniter may have become so dry as to break, allowing moisture to enter the gas vent in the igniter shell and spoil the ignition compound.	Use fresh igniters. Be sure they are not old or dried out.
In a wet hole, water may have penetrated the joint between cap and igniter fuse.	Use a cap crimper which leaves no vent. After the cap is crimped tight to the fuse, dip the entire igniter in cap-sealing compound.

Failures with electric squibs:

CAUSES	MEANS OF PREVENTION
Many of the causes listed for failures with electric detonators apply also to electric squibs and especially the fact that electric squibs may have become damp.	Keep electric squibs dry. Do not leave them lying around the mine.

Failures due to the explosive:

CAUSES	MEANS OF PREVENTION
Explosive may have become insensitive through absorption of moisture in improper storage.	Store explosives in a dry, well-ventilated magazine.
Explosive may have become insensitive through absorption of moisture in the mine, especially an ammonia explosive.	Unless approved, dry, well-ventilated magazines are provided underground, take underground only one day's supply of explosives and bring out any left over at the end of the day.
Explosive may have become insensitive through being kept too long, especially an ammonia explosive.	Use fresh explosives. Do not use discolored loose explosives or cartridges with leaky or discolored wrappers.
Explosive may have become insensitive through standing in wet holes.	In wet work use gelatin explosives. If ammonia explosives must be used in wet holes, keep the wrapper intact, waterproof the primer, and fire as soon as possible after loading.
Oil from explosive may have worked down into cap and quenched spit of fuse.	Do not use explosives from which oil is exuding. If explosive is slightly oily, crimp cap on fuse with a cap crimper which leaves no vent through which oil can enter cap.

Handling misfires. Handling a misfire is by far the most hazardous duty any blaster is called upon to perform and he should proceed with every precaution for his own safety and that of other men on the job. Misfires are much easier to prevent than to cure.

Manufacturing. Plant design and construction in explosives manufacture, which is obviously related to safety, is one of the highly specialized tasks of the chemical engineer. Location and distances are determined by some of the considerations which govern storage centers, but also, of course, by such things as availability of power, raw materials, freedom from easy attack by an enemy, and decentralization; but it is usually a source of dismay to the young explosives chemist to discover the apparent remoteness and inaccessibility of his first job.

Building construction is either of light materials with only floors of masonry, or of gravel-concrete covered with earth. Partially buried buildings, once used for safety, may be succeeded by entirely subterranean constructions as the result of airplane bombing. Everywhere, however, the possibility that accidental explosion of one building may fling heavy missiles to cause serious distant damage or explosions in others is important. Buildings where explosions are likely to occur are always barricaded with earth walls, which may be 30 feet thick at the base and 4 feet thick at the top, extending to the roof of the building or above, and planted with grass, shrubs, and trees to hold them down, against weathering. Zigzag tunnels connect buildings through barricades, but even a tunnel connection may be dangerous, as a source of propagation of explosion by influence. When materials go from one building to another, connections are often only temporary and are broken when not actually in use.

The number of buildings naturally depends on the size of the plant and, as has been indicated, plants are often very large. As a rule only one operation is carried out in one building, and many buildings may be devoted to the same operation to avoid handling too large amounts in the same one. Considerations of tools, conduct, and handling are very similar to those which have already been discussed, and there are further specific regulations with respect to each operation which is conducted.

Certain operations in all explosives industry are very hazardous; so are all operations with some explosives; and any industrial explosives operation presents some hazards. Nearly all the larger ones are carried on with the use of specialized safety devices and construction, some of which have been mentioned. Nitration is practically always dangerous and requires careful control; nitroglycerine is exceptionally hazardous until after the mixing operation. The initiator explosives are exceptionally hazardous at all times. Loading and packing operations which are done by pouring, extrusion, or tamping are not always as hazardous as might be supposed and are frequently done by women or relatively inexperienced workers.

In years gone by much emphasis was placed upon wood and on such soft metals as lead and copper for the construction of machinery for handling explosives, in view of the risks of sparks and of missile formation. These considerations are still important in certain operations, and are usually still strongly emphasized abroad. The use of iron and steel has always been extensive in the United States and is increasing.

In addition to the usual hazards of fire as in other industries, weather is often an important factor. Operations are often discontinued during thunder and lightning storms, and climatic conditions may influence efficiency of operations.

The Explosives Laboratory. Beyond the information given at various points in this book, laboratory procedure should be governed by the best judgment of an informed and competent chemist in the light of all the information he can assemble.

For teaching purposes, many plant practices may be used to govern laboratory conduct, and it must be emphasized that procedures of this kind are in many cases not merely pedagogy or play, but essential safety measures. Among them these should be specially emphasized: protection for the eyes, serious and thoughtful conduct and the elimination of casual activities, literal and exact obedience of instructions, knowledge of specific behavior of the materials used, storage under prescribed conditions, and suitable destruction of residues. The instructor must make a careful selection of the work a student is permitted to do, which will be determined by the level which the class has reached, and all instruction, if it is to be both effective and safe, must be highly individualized. With many students working in one laboratory, a careful check must always be made of the experiments which are being simultaneously conducted. Certain operations where detonation is desired or possible should never be conducted in the laboratory after the class has progressed in the work to where small amounts of explosive materials begin to be in students' hands. With qualified students—*and no others should be trained!*—the effectiveness of safety practice is largely up to the instructor, because it is easy to get full student co-operation by pointing out to the class members what is true—namely that since people with this kind of training are not numerous they themselves will, if they go on, shortly be responsible for the same things; particularly in war times, there is a large demand for their services if they are competently trained.

The laboratory storage center may be conducted similarly to a real storage magazine with control equipment and records. However small the supply of explosives may be, it should never be kept in the laboratory; only the amounts required should be brought in and issued by the instructor, and a check list should be kept. If the total amount is, as ordinarily, less than 10 pounds, any distant locked room will be satisfactory. If it does not exceed 50 pounds total, a chemical vault below ground level will be suitable. Such a vault is possessed by most laboratories; it should contain no other chemicals. All storage, however, is subject to the requirements of local controlling authorities. As one approaches 50 pounds he acquires a real explosives problem, and beyond that amount, whether for laboratory purposes or any other, one has a genuine explosives magazine which must be so treated. It should be borne in mind that 50 pounds of explosives (under the proper conditions and subject to the usual considerations) can create a crater up to 7 feet in diameter, can cause death by concussion up to about 25 feet, and fragmentation at that distance will require walls of solid construction for protection, in addition to the fire hazard of the explosion flame. Within a building, therefore, stored explosives must be surrounded by substantial construction with a careful view to the immediate environment.

Research. It is somewhat strange that more specific training in explosives has not been part of the education of all research chemists, who are often doing research with explosives when they are not aware of it. In any problem, a new compound containing both nitrogen and oxygen should always be the object of suspicion; groups previously indicated have possibly explosive properties, and one may always run into a new one. Prudence would dictate the use of preliminary semimicro procedures, and the routine testing of new compounds for ignition, shock sensitivity, dropping on a hot plate, and, where there is any indication of explosive characteristics, detonation. Where the results warrant it, a procedure for proper handling should be established.

Explosives research is an attractive and useful chemical field. As an introduction to research a bibliography is presented in the Appendix. A section on explosives, now known as Section 24, Explosives and Explosions, has been part of *Chemical Abstracts* since its inception, and can serve as an excellent jumping off place for the preliminary delving into the original literature.

Discussion Questions and Exercises

1. Tabulate the characteristics of explosives related to storage, given earlier in the text.

2. Make a pencil sketch of a smokeless-powder packing box.

3. Sketch a design for a smal explosives magazine.

4. Indicate how you would arrange specified explosives in the interior of your magazine.

5. Keep a record of the maximum and minimum daily temperatures of your storage room for one week.

6. What visual signs of deterioration can you think of for the various explosive materials?

7. Make the usual explosive calculations for the liquid gas explosives mentioned on page 418.

8. Take any flow sheet you have prepared, and assuming a suitable daily output, map out the number and arrangement of buildings required.

9. What are the safety regulations which govern your laboratory? If you were in charge, what changes would you make?

10. Propose three problems in explosive research in which you might be interested and obtain your instructor's opinion as to their merit.

11. Assume that you secure a position as an explosives chemist in a small plant producing T.N.T. You find it to be a new plant, with you as the only chemist, and the laboratory an empty room 20 x 30 feet. Perpare a summary of what you would do to meet the situation.

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Note: This bibliography, while not all-inclusive nor exhaustive, provides a representative list of the publications from the 16th century onward that bear on the principal topic of explosives in this volume; and also the titles of a few that bear on the special topics of analysis, internal ballistics, and ordnance. To facilitate the use of the titles given, one or both of two types of identification appear with each reference; one type is symbols, the other is references to specific pages in this text.

The symbols, which are at the left of the references, and their meanings are as follows:

E—publications that relate to the chief topic of the text, *explosives.*
H—publications that, while bearing on the chief topic of the text, *explosives,* are of specific interest in a consideration of the early *history* of explosives referred to in footnote 3 on page 3. Most of these are not readily accessible.
A—publications in which are described procedures in *analysis* that are useful in connection with the study of various topics in this volume.
B—publications in which are found further treatment of the topic of *internal ballistics* discussed in chapters 6 and 7 of this volume.
O—publications that relate to the topic of *ordnance* mentioned frequently in this volume.

The *italic* page references at the close of some of the publications refer to specific pages in this volume. These publications contain information that relates to definite statements on these pages in the text. The bibliography does not include the titles of many of the books and articles to which only limited reference is made in the text.

The only individual research papers listed are the intrinsically interesting matters of Sobrero's discovery of nitroglycerine, Bunsen's early theory of gunpowder, and one related to grain size.

A relatively small number of the titles is preceded by an asterisk. These volumes are particularly recommended in their entirety as sources of further information on the topics indicated by their titles or by the symbols preceding them.

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Tables

TABLE I

TEMPERATURE CORRECTION FOR BAROMETRIC READINGS

Temperature, °C.	Correction in Millimeters of Mercury	Temperature, °C.	Correction in Millimeters of Mercury
15°	2.0	23°	3.0
17°	2.2	24°	3.1
19°	2.5	25°	3.3
20°	2.6	26°	3.4
21°	2.8	28°	3.7
22°	2.9	30°	4.0

TABLE II

VAPOR TENSION OF WATER

Temperature, °C.	Vapor Tension in Millimeters of Mercury	Temperature, °C.	Vapor Tension in Millimeters of Mercury
10°	9.2	23°	21.1
12°	10.5	24°	22.4
15°	12.8	25°	23.8
16°	13.6	26°	25.2
17°	14.5	27°	26.7
18°	15.5	28°	28.3
19°	16.5	29°	30.0
20°	17.5	30°	31.8
21°	18.7	35°	42.1
22°	19.8		

TABLE III

SUMMARY OF CHARACTERISTICS OF EXPLOSIVES

Name	Formula	Products per Formula Weight	Qv Cal. Kg.$^{-1}$	Te °C.	f Kg. cm.$^{-2}$	V m. sec.$^{-1}$	Trautzl Exp. cc. 10g.$^{-1}$	Potential $\times 10^5$ Kg. m.
Gunpowder	$2\ KNO_3 + 3\ C + S$	$N_2 + 3\ CO_2 + K_2S$	501	2090	2970	—	30	2.1
Nitrocellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5\ CO + 3.5\ CO_2 + 14.5\ H_2O + 5.5\ N_2$	1250	2800	10,000	6100	420	5.3
Nitroglycerine	$C_3H_5(NO_3)_3$	$3\ CO_2 + 2.5\ H_2O + 1.5\ N_2 + .25\ O_2$	1526	3360	9835	8500	590	6.5
Ammonium Nitrate	NH_4NO_3	$2\ H_2O + N_2 + .5\ O_2$	384	1100	5100	4100	300	1.6
T.N.T.	$C_7H_5(NO_2)_3$	$6\ CO + C + 2.5\ H_2 + 1.5\ N_2$	656	2200	8386	6800	260	2.8
Picric Acid	$C_6H_2(OH)(NO_2)_3$	$6\ CO + H_2O$ $.5\ H_2 + 1.5\ N_2$	847	2717	9960	7000	300	3.6
Ammonium Picrate	$C_6H_2(NO_2)_3ONH_4$	$6\ CO + H_2O + 2\ H_2 + 2\ N_2$	622	1979	8537	6500	230	2.6
Tetryl	$C_7H_5N_5O_8$	$7\ CO + H_2O + 1.5\ H_2O + 2.5\ N_2$	908	2781	10,830	7229	320	3.9
Mercury Fulminate	$Hg(ONC)_2$	$Hg + 2\ CO + N_2$	420	4105	5212	3920	213	1.8
Lead Azide	$Pb\ N_6$	$Pb + 3\ N_2$	684	3180	8070	5000	250	2.9

TABLE IV

SULPHURIC ACID

Specific Gravity of Aqueous Solutions at 20°/4° C.*

° B.	Specific Gravity	Per Cent H_2SO_4	Grams per Liter	Pounds per Cubic Foot	Pounds per Gallon
0.7	1.0051	1	10.05	0.6275	0.0839
1.7	1.0118	2	20.24	1.263	0.1689
2.6	1.0184	3	30.55	1.907	0.2550
3.5	1.0250	4	41.00	2.560	0.3422
4.5	1.0317	5	51.59	3.220	0.4305
5.4	1.0385	6	62.31	3.890	0.5200
6.3	1.0453	7	73.17	4.568	0.6106
7.2	1.0522	8	84.18	5.255	0.7025
8.1	1.0591	9	95.32	5.950	0.7955
9.0	1.0661	10	106.6	6.655	0.8897
9.9	1.0731	11	118.0	7.369	0.9851
10.8	1.0802	12	129.6	8.092	1.082
11.7	1.0874	13	141.4	8.825	1.180
12.5	1.0947	14	153.3	9.567	1.279
13.4	1.1020	15	165.3	10.32	1.379
14.3	1.1094	16	177.5	11.08	1.481
15.2	1.1168	17	189.9	11.85	1.584
16.0	1.1243	18	202.4	12.63	1.689
16.9	1.1318	19	215.0	13.42	1.795
17.7	1.1394	20	227.9	14.23	1.902
18.6	1.1471	21	240.9	15.04	2.010
19.4	1.1548	22	254.1	15.86	2.120
20.3	1.1626	23	267.4	16.69	2.231
21.1	1.1704	24	280.9	17.54	2.344
21.9	1.1783	25	294.6	18.39	2.458
22.8	1.1862	26	308.4	19.25	2.574
23.6	1.1942	27	322.4	20.13	2.691
24.4	1.2023	28	336.6	21.02	2.809
25.2	1.2104	29	351.0	21.91	2.929
26.0	1.2185	30	365.6	22.82	3.051
26.8	1.2267	31	380.3	23.74	3.173
27.6	1.2349	32	395.2	24.67	3.298
28.4	1.2432	33	410.3	25.61	3.424
29.1	1.2515	34	425.5	26.56	3.551
29.9	1.2599	35	441.0	27.53	3.680
30.7	1.2684	36	456.6	28.51	3.811
31.4	1.2769	37	472.5	29.49	3.943
32.2	1.2855	38	488.5	30.49	4.077
33.0	1.2941	39	504.7	31.51	4.212
33.7	1.3028	40	521.1	32.53	4.349
34.5	1.3116	41	537.8	33.57	4.488
35.2	1.3205	42	554.6	34.62	4.628
35.9	1.3294	43	571.6	35.69	4.770
36.7	1.3384	44	588.9	36.76	4.914
37.4	1.3476	45	606.4	37.86	5.061
38.1	1.3569	46	624.2	38.97	5.209
38.9	1.3663	47	642.2	40.09	5.359
39.6	1.3758	48	660.4	41.23	5.511
40.3	1.3854	49	678.8	42.38	5.665
41.1	1.3951	50	697.6	43.55	5.821
41.8	1.4049	51	716.5	44.73	5.979
42.5	1.4148	52	735.7	45.93	6.140
43.2	1.4248	53	755.1	47.14	6.302
44.0	1.4350	54	774.9	48.37	6.467

* See also Tables of the Manufacturing Chemists Association of the United States. (Courtesy of the Chemical Rubber Publishing Co.)

TABLE IV (Continued)

SULPHURIC ACID

Specific Gravity of Aqueous Solutions at 20°/4° C. (*Continued*)*

° B.	Specific Gravity	Per Cent H_2SO_4	Grams per Liter	Pounds per Cubic Foot	Pounds per Gallon
44.7	1.4453	55	794.9	49.62	6.634
45.4	1.4557	56	815.2	50.89	6.803
46.1	1.4662	57	835.7	52.17	6.974
46.8	1.4768	58	856.5	53.47	7.148
47.5	1.4875	59	877.6	54.79	7.324
48.2	1.4983	60	899.0	56.12	7.502
48.9	1.5091	61	920.6	57.47	7.682
49.6	1.5200	62	942.4	58.83	7.865
50.3	1.5310	63	964.5	60.21	8.049
51.0	1.5421	64	986.9	61.61	8.236
51.7	1.5533	65	1010	63.03	8.426
52.3	1.5646	66	1033	64.46	8.618
53.0	1.5760	67	1056	65.92	8.812
53.7	1.5874	68	1079	67.39	9.008
54.3	1.5989	69	1103	68.87	9.207
55.0	1.6105	70	1127	70.38	9.408
55.6	1.6221	71	1152	71.90	9.611
56.3	1.6338	72	1176	73.44	9.817
56.9	1.6456	73	1201	74.99	10.02
57.5	1.6574	74	1226	76.57	10.24
58.1	1.6692	75	1252	78.15	10.45
58.7	1.6810	76	1278	79.75	10.66
59.3	1.6927	77	1303	81.37	10.88
59.9	1.7043	78	1329	82.99	11.09
60.5	1.7158	79	1355	84.62	11.31
61.1	1.7272	80	1382	86.26	11.53
61.6	1.7383	81	1408	87.90	11.75
62.1	1.7491	82	1434	89.54	11.97
62.6	1.7594	83	1460	91.16	12.19
63.0	1.7693	84	1486	92.78	12.40
63.5	1.7786	85	1512	94.38	12.62
63.9	1.7872	86	1537	95.95	12.83
64.2	1.7951	87	1562	97.49	13.03
64.5	1.8022	88	1586	99.01	13.23
64.8	1.8087	89	1610	100.5	13.43
65.1	1.8144	90	1633	101.9	13.63
65.3	1.8195	91	1656	103.4	13.82
65.5	1.8240	92	1678	104.8	14.00
65.7	1.8279	93	1700	106.1	14.19
65.8	1.8312	94	1721	107.5	14.36
65.9	1.8337	95	1742	108.7	14.54
66.0	1.8355	96	1762	110.0	14.70
66.0	1.8364	97	1781	111.2	14.87
66.0	1.8361	98	1799	112.3	15.02
65.9	1.8342	99	1816	113.4	15.15
65.8	1.8305	100	1831	114.3	15.28

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* See also Tables of the Manufacturing Chemists Association of the United States.
(Courtesy of the Chemical Rubber Publishing Co.)

TABLE V

NITRIC ACID

Specific Gravity of Aqueous Solutions at 20°/4° C.*

° B.	Specific Gravity	Per Cent HNO_3	Grams per Liter	Pounds per Cubic Foot	Pounds per Gallon
0.5	1.0036	1	10.04	0.6265	0.0838
1.3	1.0091	2	20.18	1.260	0.1684
2.1	1.0146	3	30.44	1.900	0.2540
2.9	1.0201	4	40.80	2.547	0.3405
3.6	1.0256	5	51.28	3.201	0.4279
4.4	1.0312	6	61.87	3.862	0.5163
5.2	1.0369	7	72.58	4.531	0.6057
5.9	1.0427	8	83.42	5.207	0.6961
6.7	1.0485	9	94.37	5.891	0.7875
7.5	1.0543	10	105.4	6.582	0.8798
8.2	1.0602	11	116.6	7.280	0.9732
9.0	1.0661	12	127.9	7.986	1.068
9.8	1.0721	13	139.4	8.701	1.163
10.5	1.0781	14	150.9	9.422	1.260
11.3	1.0842	15	162.6	10.15	1.357
12.0	1.0903	16	174.4	10.89	1.456
12.8	1.0964	17	186.4	11.64	1.555
13.5	1.1026	18	198.5	12.39	1.656
14.2	1.1088	19	210.7	13.15	1.758
15.0	1.1150	20	223.0	13.92	1.861
15.7	1.1213	21	235.5	14.70	1.965
16.4	1.1276	22	248.1	15.49	2.070
17.1	1.1340	23	260.8	16.28	2.177
17.9	1.1404	24	273.7	17.09	2.284
18.6	1.1469	25	286.7	17.90	2.393
19.4	1.1534	26	299.9	18.72	2.503
20.0	1.1600	27	313.2	19.55	2.614
20.7	1.1666	28	326.6	20.39	2.726
21.4	1.1733	29	340.3	21.24	2.840
22.1	1.1800	30	354.0	22.10	2.954
22.8	1.1867	31	367.9	22.97	3.070
23.5	1.1934	32	381.9	23.84	3.187
24.2	1.2002	33	396.1	24.73	3.305
24.9	1.2071	34	410.4	25.62	3.425
25.6	1.2140	35	424.9	26.53	3.546
26.2	1.2205	36	439.4	27.43	3.667
26.8	1.2270	37	454.0	28.34	3.789
27.5	1.2335	38	468.7	29.26	3.912
28.1	1.2399	39	483.6	30.19	4.035
28.7	1.2463	40	498.5	31.12	4.160
29.3	1.2527	41	513.6	32.06	4.286
29.8	1.2591	42	528.8	33.01	4.413
30.4	1.2655	43	544.2	33.97	4.541
31.0	1.2719	44	559.6	34.94	4.670
31.6	1.2783	45	575.2	35.91	4.800
32.1	1.2847	46	591.0	36.89	4.932
32.7	1.2911	47	606.8	37.88	5.064
33.2	1.2975	48	622.8	38.88	5.197
33.8	1.3040	49	639.0	39.89	5.332
34.3	1.3100	50	655.0	40.89	5.466

* See also Tables of the Manufacturing Chemists Association of the United States. (Courtesy of the Chemical Rubber Publishing Co.)

TABLE V (Continued)

NITRIC ACID

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS AT 20°/4° C.*

Specific Gravity of Aqueous Solutions at 20°/4° C.(*Continued*)*

° B.	Specific Gravity	Per Cent HNO$_3$	Grams per Liter	Pounds per Cubic Foot	Pounds per Gallon
34.8	1.3160	51	671.2	41.90	5.601
35.3	1.3219	52	687.4	42.91	5.736
35.8	1.3278	53	703.7	43.93	5.873
36.3	1.3336	54	720.1	44.96	6.010
36.7	1.3393	55	736.6	45.98	6.147
37.2	1.3449	56	753.1	47.02	6.285
37.6	1.3505	57	769.8	48.06	6.424
38.1	1.3560	58	786.5	49.10	6.563
38.5	1.3614	59	803.2	50.14	6.703
38.9	1.3667	60	820.0	51.19	6.843
39.3	1.3719	61	836.9	52.24	6.984
39.7	1.3769	62	853.7	53.29	7.124
40.1	1.3818	63	870.5	54.34	7.265
40.4	1.3866	64	887.4	55.40	7.406
40.8	1.3913	65	904.3	56.46	7.547
41.1	1.3959	66	921.3	57.51	7.688
41.5	1.4004	67	938.3	58.57	7.830
41.8	1.4048	68	955.3	59.63	7.972
42.1	1.4091	69	972.3	60.70	8.114
42.4	1.4134	70	989.4	61.76	8.257
42.7	1.4176	71	1006	62.83	8.399
43.0	1.4218	72	1024	63.91	8.543
43.3	1.4258	73	1041	64.98	8.686
43.6	1.4298	74	1058	66.05	8.830
43.9	1.4337	75	1075	67.13	8.973
44.1	1.4375	76	1093	68.20	9.117
44.4	1.4413	77	1110	69.28	9.262
44.7	1.4450	78	1127	70.36	9.406
44.9	1.4486	79	1144	71.44	9.550
45.1	1.4521	80	1162	72.52	9.694
45.4	1.4555	81	1179	73.60	9.839
45.6	1.4589	82	1196	74.68	9.983
45.8	1.4622	83	1214	75.76	10.13
46.1	1.4655	84	1231	76.85	10.27
46.3	1.4686	85	1248	77.93	10.42
46.5	1.4716	86	1266	79.01	10.56
46.7	1.4745	87	1283	80.08	10.71
46.8	1.4773	88	1300	81.16	10.85
47.0	1.4800	89	1317	82.23	10.99
47.2	1.4826	90	1334	83.30	11.14
47.4	1.4850	91	1351	84.36	11.28
47.5	1.4873	92	1368	85.42	11.42
47.6	1.4892	93	1385	86.46	11.56
47.8	1.4912	94	1402	87.51	11.70
47.9	1.4932	95	1419	88.56	11.84
48.0	1.4952	96	1435	89.61	11.98
48.2	1.4974	97	1452	90.67	12.12
48.4	1.5008	98	1471	91.82	12.27
48.7	1.5056	99	1491	93.05	12.44
49.2	1.5129	100	1513	94.45	12.63

* See also Tables of the Manufacturing Chemists Association of the United States. (Courtesy of the Chemical Rubber Publishing Co.)

TABLE VI

LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	10	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	11	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6386	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

TABLE VI (*continued*)

LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	2	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

TABLE VII

UNITS OF WORK AND ENERGY

British thermal unit (mean) (B.T.U.): 0.25198 kilogram-calorie or large calorie (mean); 107.56 kilogram-meters; 1,054.8 joules.

Cubic foot-atmosphere: 28.313 liter-atmospheres; 292.59 kilogram-meters; 680.74 gram-calories; 2,869.4 joules.

Erg: 2.3889×10^{-11} kilogram-calorie; 1.0197×10^{-8} kilogram-meter; 7.3756×10^{-8} foot-pound; 1×10^{-7} joule; 0.0010197 gram-centimeter; 1 dyne-centimeter.

Foot-pound: 3.7662×10^{-7} kilowatt-hour; 5.0505×10^{-7} horse-power hour; 3.2389×10^{4} kilogram-calorie (mean); 4.7253×10^{-4} cubic-foot atmosphere; 0.013381 liter-atmosphere; 0.13826 kilogram-meter; 1.3558 joule; 32.174 foot-poundals; 1.3825×10^{4} gram-centimeters; 1.3558×10^{7} ergs or centimeter-dynes.

Foot-poundal: 0.03108 foot-pound; 0.042140 joule; 4.2140×10^{5} ergs.

Gram-calorie (mean): 1.5993×10^{-6} horsepower hour; 0.001 kilogram-calorie; 0.0011628 watt-hour; 0.001469 cubic-foot-atmosphere; 0.041311 liter-atmosphere; 0.42685 kilogram-meter; 3.0874 foot-pounds; 4.186 joules.

Gram-centimeter: 2.3427×10^{-8} kilogram-calorie; 1×10^{-5} kilogram-meter; 7.233×10^{-5} foot-pounds; 9.8067×10^{-5} joule; 980.7 ergs.

Horsepower hour (h.p.hr.).: 0.7457 kilowatt hour; 641.30 kilogram-calories; 2.7374×10^{5} kilogram-meters; 1.9800×10^{6} foot-pounds; 2.6845×10^{6} joules.

International volt-electronic charge: 1.5927×10^{-19} joule.

Joule (absolute): 2.778×10^{-7} kilowatt-hour; 3.725×10^{-7} horsepower hour; 2.3889×10^{-4} kilogram-calorie; 3.485×10^{-4} cubic-foot atmosphere; 0.009869 liter-atmosphere; 0.10197 kilogram-meter; 0.73756 foot-pound; 0.99968 joule; 1 watt-second; 1.0197×10^{4} gram-centimeters; 1×10^{7} ergs.

Kilogram-calorie or large calorie (mean): 0.0011628 kilowatt-hour; 0.0015593 horsepower-hour; 426.85 kilogram-meters; 1,000 small or gram-calories; 3,087.4 foot-pounds; 4,186 joules; 4.2686×10^{7} gram-centimeters; 4.186×10^{10} ergs.

Kilogram-meter: 2.7235×10^{-6} kilowatt-hour; 3.6530×10^{-6} horsepower hour; 0.0034177 cubic-foot atmosphere; 0.096782 liter-atmosphere; 2.3427 gram-calories; 7.2330 foot-pounds; 9.80665 joules; 1×10^{5} gram-centimeters; 9.80665×10^{7} ergs.

Kilowatt-hour: 1.3410 horsepower-hours; 1,000 watt hours; 3.6710×10^{5} kilogram-meters; 8.6001×10^{5} gram-calories; 2.6552×10^{6} foot-pounds; 3.6000×10^{6} joules.

Large calorie: See *kilogram calorie.*

Liter-atmosphere: 10.333 kilogram-meters; 24.206 gram-calories; 74.735 foot-pounds; 101.33 joules.

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UNIVERSITY OF WISCONSIN

INTERNATIONAL ATOMIC WEIGHTS

1941

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atom Weig
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.
Argon	A	18	39.944	Neon	Ne	10	20.18
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.00
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.00
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.2
Calcium	Ca	20	40.08	Potassium	K	19	39.0
Carbon	C	6	12.010	Praseodymium	Pr	59	140.9
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	
Copper							

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